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ON A THEORY OF THE ACTION OF RECTANGULAR SHORT-WAVE FRAME AERIALS

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ABSTRACT. In a previous approximate theory of the action of rectangular frame aerials used with waves comparable in length to the frame-dimensions, it was assumed that the frame current would be a maximum when the initial current produced by a local oscillator or a passing electromagnetic wave was in phase with a supplementary current produced by the mutual reactions between the currents in opposite limbs of the frame. The co-phasing of these component currents was accomplished by adjusting the dimensions of the frame, a process for which the term "formatizing" was suggested.

The present paper develops this theory, and the critical dimensions for rectangular transmitting and receiving frames are exactly determined. It is found that the maximum error arising from the use of the approximate formulae previously given does not exceed 1·7 per cent and is usually less than 3 per cent. These errors are not greater than the experimental errors which arise when short waves comparable in length to the dimensions of the frames are used.

§ 1. THE ACTION OF RECTANGULAR SHORT-WAVE FRAMES

A CURRENT is generally produced in a wireless frame aerial either because the frame is fed by a local high-frequency oscillator or because passing electromagnetic waves are incident upon it. Either of these primary sources of energy will cause an initial current to be set up in the frame. If the frame be rectangular and if its dimensions be comparable with the wave-length of the initial current, then two other supplementary or component currents (which are otherwise negligible) will contribute appreciably to the final or resultant current produced in the frame.

One of these supplementary currents is due to the fact that the initial current in one limb of the frame at any point P, say, contributes to the resultant current in the opposite limb of the frame at P', say, by direct radiation across the frame, whilst the

initial current at P also contributes to the resultant current at P by reflection of it radiation back to P from the opposite limb of the frame.

The other supplementary current arises from the fact that the initial disturbanc at P causes a wave to travel round the frame-perimeter back to P where it, also, wi contribute to the initial disturbance.

In the previous communications [1,2,3] an approximate theory of the first o radiation effect has been given, whilst the second effect has been discussed in paper on the current-distribution round a short-wave frame aerial [4]. It is th object of the present note to consider the magnitude of the errors arising from th approximate theory of the radiation effect which has been described in the com munications [1,2,3] referred to above.

§ 2. THEORETICAL CONSIDERATIONS: TRANSMISSION

Consider first the case of a frame actuated by a local oscillator, and let the initia

I, I_0, ω current per centimetre at P in one limb of the frame be I, where $I = I_0 \sin \omega t$. Thi initial current will not be that actually measured because it will be more or les reinforced by the supplementary currents produced by the radiation effects referre to above. In the case of a transmitting frame, let this initial current I at P produc

i, i_0, ρ_t a supplementary current i at P given by $i = i_0 \sin(\omega t + \rho_t)$ per centimetre and als

i' a supplementary current i' at P', in the opposite limb of the frame, given b

i_0', ρ_t' $i' = i_0' \sin(\omega t + \rho_t')$ per centimetre. The amplitudes i_0 and i_0' are dependent on I_0

λ, D on the wave-length λ in air, and on the distance D between the opposite limbs o the frame. ρ_t and ρ_t' are phase-changes between i and i' respectively and the initia current I. These phases are dependent on both time and space. We may write th supplementary currents in the general form

$$f(\lambda D)\, I_0 \sin [\omega t + 2\pi \int (\nu\, dt - ds/\lambda)],$$

ν, t, s where ν is the wave frequency and dt and ds are increments of time and spac respectively. The initial and supplementary currents at P will have a resultan

I_R current I_R, the amplitude of which will depend on the amplitudes of and the phase difference between the component currents. If i_0 and i_0' were constant and in dependent of D, then, for a given wave-length, a maximum resultant current woul occur when the components I and i at P were in phase and when the component I at P and i' at P' were π out of phase. The approximate theory already give assumed that for a given wave-length the variation of i_0 or i_0' with D was negligibl for values of D not very different from that particular value for which the tw components were in or out of phase. Thus it was concluded* that the fram current would be a maximum when

$$\rho_t = \pm 2n\pi \qquad \ldots\ldots(1a)$$

and

$$\rho_t' = \pm (2n' + 1)\, \pi \qquad \ldots\ldots(1b),$$

n, n' where n and n' are integers.

For the particular case of a transmitting frame the two components I and recombine at P after a time interval $2t$, say, during which the initial component

* See references (2) and (1) respectively.

at P has continued, whilst the supplementary component i at P has resulted from radiation which has travelled across the frame and back through a total distance of $2D$. Thus at point P and time $2t$ the initial component I has suffered a phase-change of $2\pi.2\nu t$ whilst the supplementary component i has also suffered a phase-change of $2\pi.2\nu t$ together with other phase-changes due to the distance $2D$ and to the mechanism of emission and absorption of radiation by the limbs of the frame. Thus the resultant phase-change may be considered as that due to the time interval $2t$ together with that due to the "effective" distance traversed by the radiation.

It has been shown[1,2,3] that this "effective" distance is given by

$$2\left(D-\frac{\lambda}{2\pi}\tan^{-1}\frac{a^2-1}{a}\right),$$

where $a=2\pi D/\lambda$. Hence, for the case of a transmitting frame, the phase-difference between the supplementary current i at P and the initial current I at P is given by

$$\begin{aligned}\rho_t &= 2\pi\left\{2\left[\nu t-\frac{1}{\lambda}\left(D-\frac{\lambda}{2\pi}\tan^{-1}\frac{a^2-1}{a}\right)\right]-2\nu t\right\}\\ &= -2\,(a-\phi),\end{aligned}$$

where $\phi=\tan^{-1}\dfrac{a^2-1}{a}$. If the assumption that $\rho_t=\pm 2n\pi$ be correct, then we have

$$-2\,(a-\phi)=\pm 2n\pi$$

or

$$\tan\,(a\pm n\pi)=(a^2-1)/a \qquad \ldots\ldots(2a).$$

Similarly the two components at P' will recombine after a time interval t during which the supplementary component i' will have resulted from radiation which has travelled across the frame a distance D. Thus the phase-difference between the supplementary current i' at P' and the initial current I at P is ρ_t', where

$$\begin{aligned}\rho_t' &= 2\pi\left\{\left[\nu t-\frac{1}{\lambda}\left(D-\frac{\lambda}{2\pi}\tan^{-1}\frac{a^2-1}{a}\right)\right]-\nu t\right\}\\ &= -(a-\phi).\end{aligned}$$

Hence, if $\rho_t'=\pm(2n'+1)\,\pi$, we have

$$\tan\,[a\pm(2n'+1)\,\pi]=(a^2-1)/a \qquad \ldots\ldots(2b).$$

Since $\rho_t=2\rho_t'$ these equations—and equations (1)—can only be satisfied simultaneously if n be an odd integer. Consequently, only alternate solutions of equation $(2a)$ give what were, for convenience of reference, called the first formatizing conditions for transmission,* that is, the conditions giving the critical dimensions of the frame for maximum current from a local oscillator of constant voltage output. By introducing the arbitrary parameter ψ the final formatizing conditions for rectangular transmitting frames were given as

$$\left.\begin{aligned}\tan\,(a-\psi)&=(a^2-1)/a\\ \text{and}\quad \tan\,(a'+\psi)&=(a'^2-1)/a'\end{aligned}\right\} \qquad \ldots\ldots(3),$$

where $a=2\pi W/\lambda$ and $a'=2\pi H/\lambda$, W and H being the frame-width and height respectively.

* See reference (2), p. 66.

It is now desirable to examine the function $f(\lambda D)$ in order to see how i_0 and i_0' vary with D. This will enable us to determine to what extent the assumptions underlying equations (1) and (2) are justified and will also enable the magnitude of the errors involved in equations (3) to be calculated.

If the initial current at P in one limb of the rectangular frame be $I_0 \sin \omega t$ per cm., then the supplementary current i' per cm. produced in the parallel opposite limb a distance D away is given by the equation

$$i' = \frac{J \cdot I_0}{D^3} \sqrt{[(a^2-1)^2+a^2]} \sin [\omega t - (a-\phi)],$$

J where J is a constant.* For convenience of calculation this expression may be written in the form

$$\begin{aligned} i' &= KI_0 \sqrt{(1/a^2 - 1/a^4 + 1/a^6)} \sin [\omega t - (a-\phi)] \\ &= i_0' \sin (\omega t + \rho_t'). \end{aligned}$$

K Here K is another constant for a given wave-length. With i' in amperes per centi-
R metre and D and λ in centimetres, the constant $K = 120\pi^2/\lambda^2 R$, where R is the resistance in ohms per centimetre of the frame wire. The numerical value of K for the short waves under consideration and for suitable copper wire is of the order of unity.† It is shown below that the exact value of K is of little importance in connection with the present problem.

The field radiated by the current i' is responsible for producing the supplementary current i at P in the original wire. The relation between i' and i will be similar to that between I and i', and consequently

$$\begin{aligned} i &= Ki_0' \sqrt{(1/a^2 - 1/a^4 + 1/a^6)} \sin [\omega t - 2(a-\phi)] \\ &= K^2 (1/a^2 - 1/a^4 + 1/a^6) I_0 \sin [\omega t - 2(a-\phi)] \\ &= i_0 \sin (\omega t + \rho_t) \qquad \text{.....(4).} \end{aligned}$$

For convenience in determining the magnitude of the errors involved in the use of equations (1) or (2), the discussion will be restricted to a consideration of the supplementary current i at P, although the same results can be obtained by considering the supplementary current i' at P'.

In figure 1, $i_0/K^2 I_0$ is plotted against a (i.e. $2\pi D/\lambda$), whilst ρ_t is plotted against a in the full-line graph of figure 2. By plotting corresponding data from these two graphs, the spiral vector diagram of figure 3 is obtained. Figure 3*b* is figure 3*a* enlarged. Any point on this spiral, when multiplied by the scalar constant $K^2 I_0$, represents vectorially the supplementary current i for any particular value of a. In the theory already given any small element of this spiral was assumed to be part of a circle for values of a greater than about 1·25, i.e. for values of D greater than 0·2λ. If this were true, it is obvious that the resultant current I_R would be greatest when

* See reference (1), p. 195, where the nomenclature is slightly different from that used in the present paper.

† According to some recent measurements by Walmsley (*J. Instn elect. Engrs*, **69**, 311) the resistance per cm. of 1/0·044 copper wire for a wave-length of about 15 metres is 0·0055 Ω. approximately. Therefore for this wire $K = 0{\cdot}6$.

its components I and i were exactly in phase, and equations (2a) and (3) would be justified. Because i_0 is a function of D (for a constant wave-length) these equations are only approximately true, and the exact value of the amplitude of I_R, the resultant current, is given by

$$_0I_R=\sqrt{[I_0^2+i_0^2+2I_0i_0\cos 2\,(a-\phi)]} \qquad \text{.....(5).}$$

$_0I_R$

On substituting in equation (5) the value of i_0 given in equation (4), we get

$$_0I_R=I_0\sqrt{[1+K^4\,(1/a^2-1/a^4+1/a^6)^2+2K^2\,(1/a^2-1/a^4+1/a^6)\cos 2\,(a-\phi)]}.$$

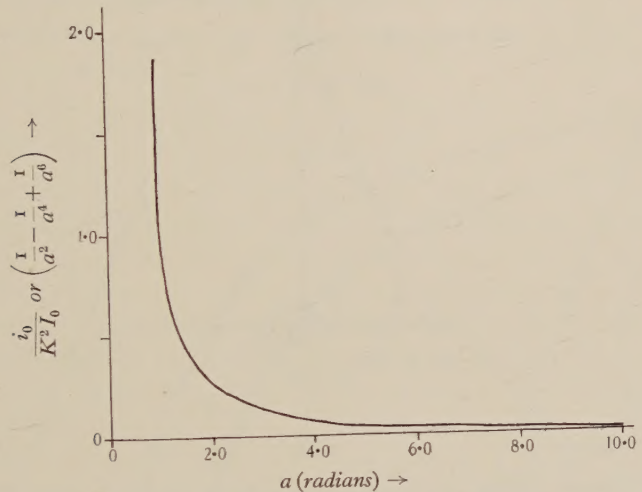

Figure 1. Graph showing the variation in amplitude of the first supplemental current.

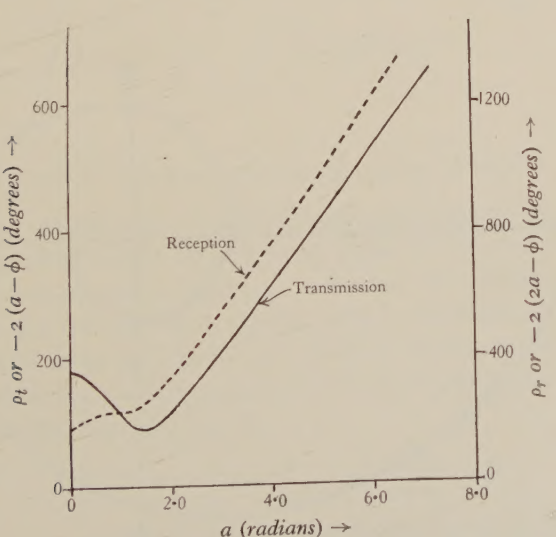

Figure 2. Graph showing the variation in phase of the first supplemental current.

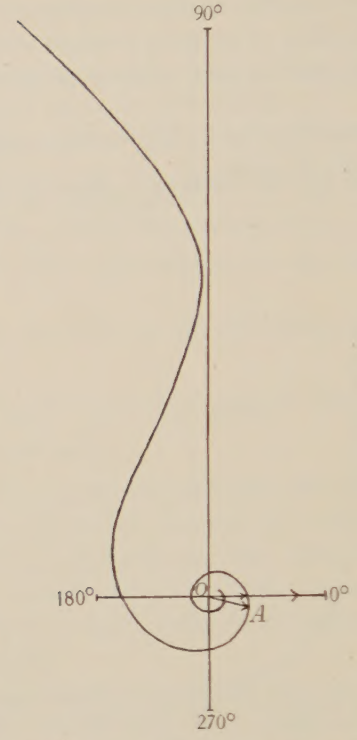

Figure 3*a*. Vector diagram showing the variation in amplitude and phase of the first supplemental current in transmission.

$$r=\left(\frac{1}{a^2}-\frac{1}{a^4}+\frac{1}{a^6}\right), \quad \theta=-2\,(a-\phi).$$

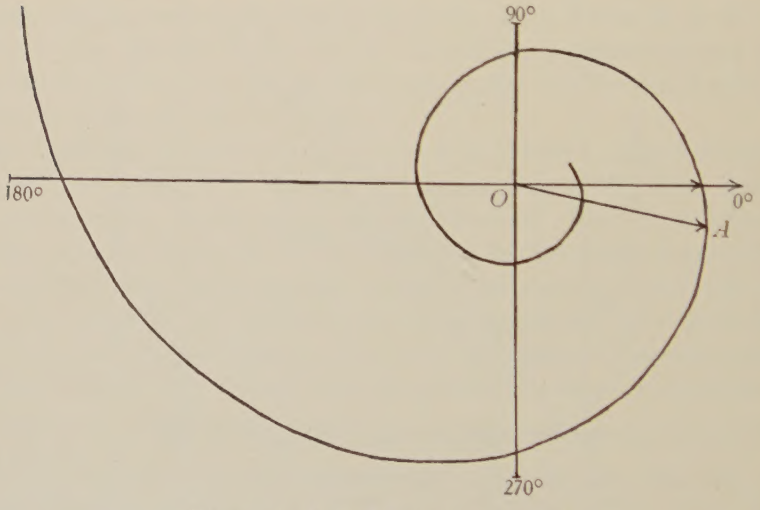

Figure 3*b*. Part of figure 3*a* enlarged.

On equating $d\,({}_0I_R)/d\,(a)$ to zero we get the conditions for maximum or minimum resultant current at the point P in the frame, namely

$$-2\,(a-\phi)=\left\{\tan^{-1}\left[\frac{1}{a}-\frac{2}{a\,(a^2-1)^2}\right]+\sin^{-1}\frac{K^2\,[(a^2-1)^2+2]\,[(a^2-1)^2+a^2]}{a^6\sqrt{[(a^2-1)^2+2]^2+[a\,(a^2-1)^2]^2}}\right\}\pm 2n\pi$$

$$=\tan^{-1}A+\sin^{-1}B\pm 2n\pi \qquad \text{.....(6).}$$

This may be compared with equation (2*a*) which is

$$-2\,(a-\phi)=\pm 2n\pi.$$

In order to solve these transcendental equations it is convenient to write them respectively in the form

$$a\pm n\pi=\phi-\tfrac{1}{2}\,(\tan^{-1}A+\sin^{-1}B)$$

and

$$a\pm n\pi=\phi.$$

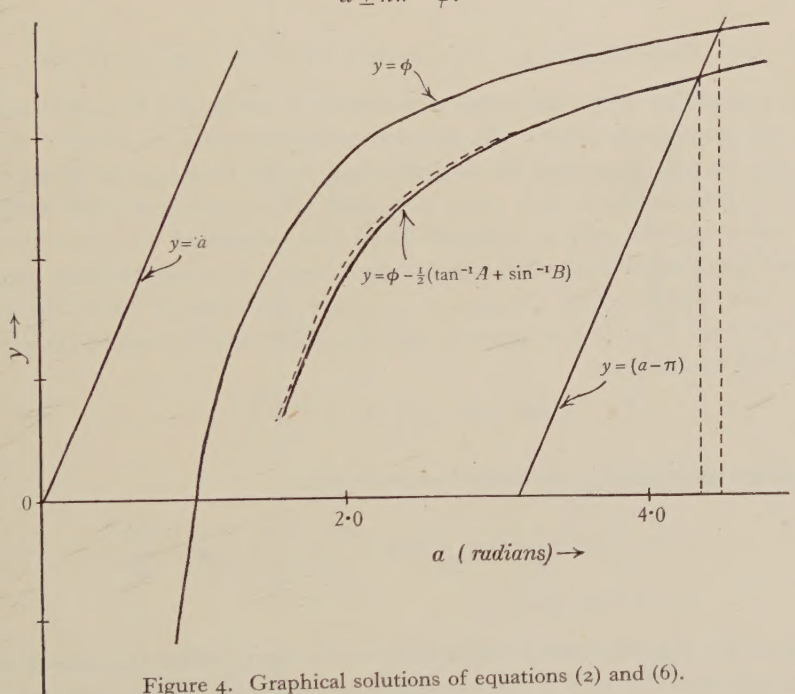

Figure 4. Graphical solutions of equations (2) and (6).

Then the solutions are obtained where the straight lines $y=a\pm n\pi$ intersect the curves $y=\phi-\tfrac{1}{2}\,(\tan^{-1}A+\sin^{-1}B)$ and $y=\phi$ respectively. For values of K equal to 1 these graphs are shown in figure 4, and from the alternate points of intersection the values of a for maximum current may be determined. The approximate equations (2) give a value of D/λ (or $a/2\pi$) equal to 0·713, the value previously given; whilst the first solution of equation (6) is $D/\lambda=0{\cdot}694$. An approximation to equation (6) better than equation (2) is

$$-2\,(a-\phi)\fallingdotseq\left(\tan^{-1}\frac{1}{a}+\sin^{-1}\frac{K^2}{a^3}\right)\pm 2n\pi \qquad \text{.....(7).}$$

The graph of $y=\phi-\tfrac{1}{2}\,(\tan^{-1}a^{-1}+\sin^{-1}a^{-3})$ is shown by the dotted curve in figure 4, and the resulting critical values of D/λ are hardly distinguishable from those

given by equation (6). The very small value of the arc sin term shows that the correcting factor is practically independent of the precise value of K as long as K does not differ greatly from unity.*

On substituting 0·694 for D/λ in equation (6) we get the value of the correcting term $\frac{1}{2}(\tan^{-1} A + \sin^{-1} B)$ which is found to be equal to 12·8°. Thus the decrease in I_R due to this phase angle between the components I and i is more than compensated by the increased value of the amplitude of i (i.e. i_0); whilst, for phase angles greater than 12·8°, the further increase in i_0 is insufficient to compensate for the reduction in I_R arising from the larger phase-difference between its component currents. This critical value of i_0 (divided by the scalar constant $K^2 I_0$) is shown in figure 3 by the vector OA.

§ 3. THEORETICAL CONSIDERATIONS: RECEPTION

With a receiving frame the initial disturbance at any point P is produced by an incident electromagnetic wave. The supplementary currents i at P and i' at P' due, respectively, to reflection from the opposite limb of the frame or to radiation across the frame will be identical with those discussed above for the transmitting frame; but the initial current will be different from that produced by a local oscillator. The initial disturbance at P, with which i combines, is produced by that part of the incident wave which was a distance $-2D$ from the point P when the reflected radiation first left P at time $2t$ seconds ago. Thus the current I due to this retarded potential will be given by

$$I_0 \sin\left[\omega t + 2\pi\left(2\nu t - \frac{-2D}{\lambda}\right)\right]$$

ρ_r and the phase-difference ρ_r between I and i is now

$$\rho_r = 2\pi\left\{\left[2\nu t - \frac{2}{\lambda}\left(D - \frac{\lambda}{2\pi}\tan^{-1}\frac{a^2-1}{a}\right)\right] - \left(2\nu t + \frac{2D}{\lambda}\right)\right\}$$
$$= -2(2a - \phi).$$

The phase of the supplementary component i is the term within the square brackets and is the same as in the case of the transmitting frame. Hence the resultant current I_R at P has an amplitude ${}_0I_R$ given by

$${}_0I_R = \sqrt{[I_0^2 + i_0^2 + 2I_0 i_0 \cos 2(2a - \phi)]} \qquad \ldots\ldots(8)$$

in which, from equation (4),

$$i_0 = K^2 I_0 (a^{-2} - a^{-4} + a^{-6}).$$

The way in which ρ_r changes with a is shown in the dotted graph of figure 2, and from this graph and figure 1 the spiral vector diagram of figure 5 has been drawn.

On substituting in equation (8) for i_0 as before, and equating the differential with respect to a to zero, we get equation (9), the odd solutions of which will give the values of D/λ for maximum receiving frame current:

* See footnote † on p. 380.

$$-2(2a-\phi)=\left\{\tan^{-1}\left[\frac{1}{2a}-\frac{a^2-4}{4a(a^2-1)^2+2a^3}\right]\right.$$
$$\left.+\sin^{-1}\frac{K^2[(a^2-1)^2+2][(a^2-1)^2+a^2]}{a^6\sqrt{[\{(a^2-1)^2+2\}^2+\{2a(a^2-1)^2+a^3\}^2]}}\right\}\pm 2n\pi \quad \ldots\ldots(9)$$
$$=\tan^{-1}A'+\sin^{-1}B'\pm 2n\pi. \qquad A', B'$$

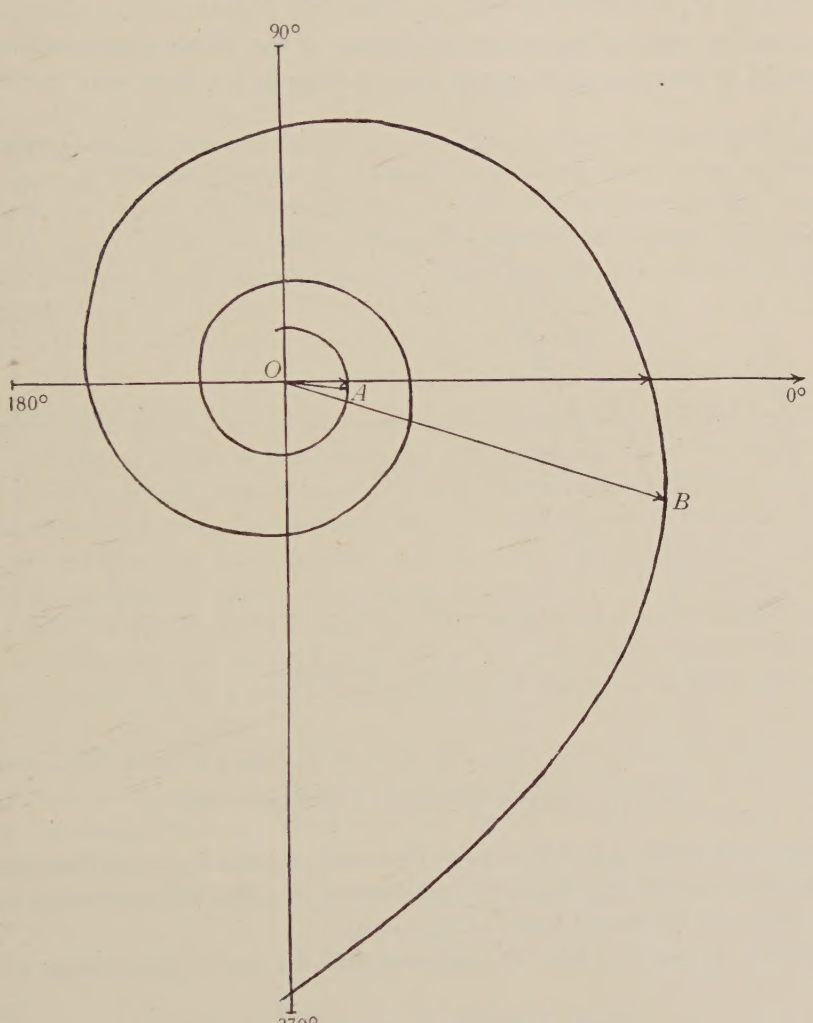

Figure 5. Vector diagram showing the variation in amplitude and phase of the first supplemental current in reception.

$$r=\left(\frac{1}{a^2}-\frac{1}{a^4}+\frac{1}{a^5}\right), \quad \theta=-2(2a-\phi).$$

The equations previously deduced on the assumption that I_R is a maximum when I and i are in phase[2,3] and when I and i' are out of phase[1] were

$$\rho_r=-2(2a-\phi)=\pm 2n\pi \qquad \ldots\ldots(10a)$$

and

$$\rho_r'=-(2a-\phi)=\pm(2n'+1)\pi \qquad \ldots\ldots(10b).$$

W, H, γ

By introducing an arbitrary phase angle ψ and also the effective frame-width $W\cos\gamma$ and the effective frame-height $H\sin\gamma$ for waves incident at an angle γ to the frame, the formatizing conditions for rectangular receiving frames were given by

$$\left.\begin{aligned}\tan\left[a\left(1+\cos\gamma\right)-\psi\right]&=(a^2-1)/a\\ \text{and}\qquad \tan\left[a'\left(1+\sin\gamma\right)+\psi\right]&=(a'^2-1)/a'\end{aligned}\right\} \qquad \ldots\ldots(11),$$

where a and a' refer to the width and height of the frame respectively. With γ and ψ equal to zero, the solutions of these equations for maximum currents are

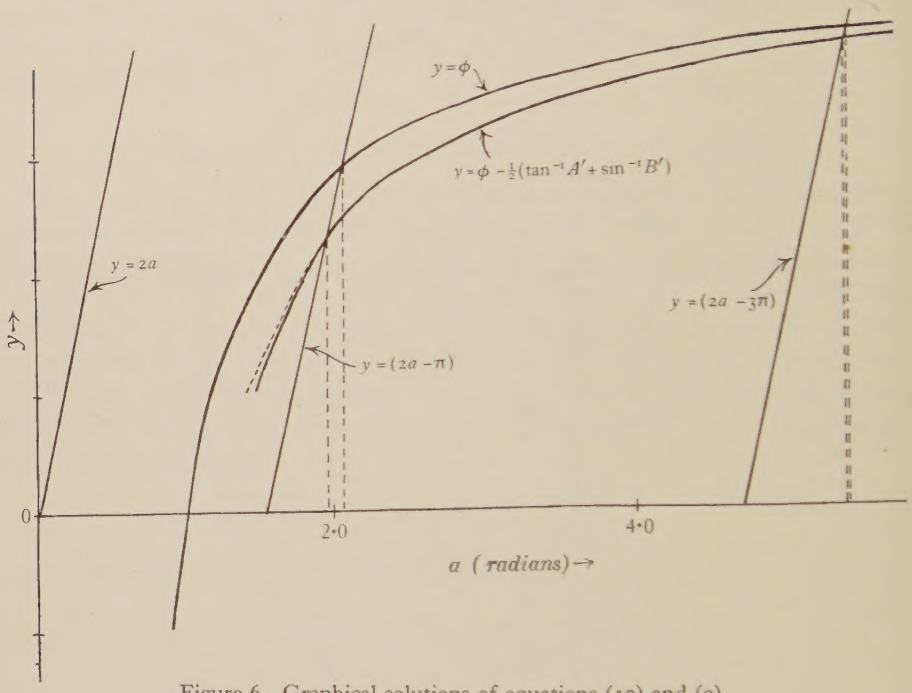

Figure 6. Graphical solutions of equations (10) and (9).

$W/\lambda=0{\cdot}331$ and $0{\cdot}860$ and $H/\lambda=0{\cdot}713$. This result for the value of H/λ is the same as that for the transmitting frame because, when $\gamma=0$, the incident wave does not directly affect the horizontal limbs of the frame.

Equations (9) and (10) may be compared with the useful approximate equation

$$-2\left(2a-\phi\right)\fallingdotseq\left(\tan^{-1}\frac{1}{2a}+\sin^{-1}\frac{K^2}{2a^3}\right)\pm 2n\pi \qquad \ldots\ldots(12).$$

The first two solutions of equations (9) and (10) for maximum current are shown in figure 6, in which the dotted curve represents the graph of the equation

$$y=\phi-\frac{1}{2}\left(\tan^{-1}\frac{1}{2a}+\sin^{-1}\frac{1}{2a^3}\right).$$

As before, the value of K within practical limits does not appreciably alter the correction factor.

The straight lines are the graphs of $y=(2a\pm n\pi)$. The solutions previously obtained from equation (10) or equation (11), namely $D/\lambda=0{\cdot}331$ and $0{\cdot}860$, may now be compared with the new results from equation (9). These are $D/\lambda=0{\cdot}316$ and $0{\cdot}856$ when $n=1$ and 3 respectively.

On substituting these new values in equation (9), the correcting terms on the right-hand side are found to be $18{\cdot}0°$ and $8{\cdot}4°$ respectively. Thus the critical values of i which, together with I, will give a maximum resultant current are

$$i_0 \sin(\omega t - 342°) \quad \text{and} \quad i_0 \sin(\omega t - 1071{\cdot}6°)$$

respectively. These supplementary currents are proportional to the vectors OB and OA in figure 5. Alternate points of intersection must be taken because, when the component currents at P differ by 4π, 8π, 12π, etc. and satisfy equation (10*a*) they differ at P' by 2π, 4π, 6π, etc. which is not in agreement with equation (10*b*). This point was referred to in the discussion of equation (2*a*) in connection with the transmitting frame.

§ 4. CONCLUSION

Experimental measurements of the critical or formatizing dimensions of transmitting and receiving frames (for which the frame currents attain maximum values for given input voltage) yield values of D/λ which agree closely with those calculated from the theoretical formulae discussed above, but the errors of measurements are usually greater than the errors arising from the use of the approximate equations (2) and (10) instead of equations (6) and (9) respectively. The percentage error in the first value of D/λ given by equations (2) or (3) is 2·8 per cent, whilst the errors of the first two solutions of equations (10) or (11) are 4·75 per cent and 0·47 per cent respectively. These errors are independent of the value of K for all practical frames.

It would therefore appear that the best shapes of rectangular short-wave frames for transmission and reception (that is, the critical dimensions for formatized frames) may be calculated with sufficient accuracy for all practical purposes from the theoretical equations (2) and (10) based on the co-phasing of the initial and supplementary currents, whilst for more accurate calculations equations (7) and (12) are useful.

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(2) Palmer and Taylor. *Proc. phys. Soc.* **46**, 62 (1934).
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THE CURRENT VARIATIONS IN A SHORT-WAVE SQUARE FRAME AERIAL REVOLVING IN ITS OWN PLANE

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ABSTRACT. From a theory of the action of short-wave frame aerials outlined in previous communications it was concluded that the current at any point in a rectangular frame aerial should vary with time as the frame revolved in its own plane. If the current-measuring instrument moves round with the frame, complications arise because the instrument records not only the current-variations due to changes in what was called the degree of formatization of the frame, but also those due to the fact that the instrument passes in succession through the current nodes and antinodes which have been shown to be fixed in space and not to revolve with the frame. Hence current-measurements have been made, firstly with the frame fixed and the instrument moving round the frame, and secondly with the instrument fixed in space as the frame revolved. The apparatus and methods employed are briefly described. The current-variations observed in the two sets of experiments conform approximately to those predicted from the theory. The results lead in general to the conclusion that when a square frame aerial is used with short waves and revolves in its own plane then, in addition to spatial current-variations round the perimeter of the frame due to the formation of fixed current nodes and antinodes, there may also be temporal current variations at any fixed point due to the fact that the frame may become alternately formatized and deformatized as it revolves.

§ 1. INTRODUCTION

According to the familiar view that the e.m.f. in a receiving frame aerial is proportional to the rate of change of the magnetic flux interlinked with it, the current should vary as the frame rotates about an axis in its plane, but there should be no current variations as a receiving frame revolves about an axis perpendicular to its plane, that is, as the frame revolves in its own plane.

It has, however, been shown[1] that current variations are to be expected in the latter case if the frame be rectangular and if its dimensions be comparable with the length of the wave. This arises because other factors are involved which modify the simple theory indicated above. In particular, at any point in the frame the e.m.f. not only is produced by the changing magnetic flux of the incident wave, but also is influenced firstly by radiation from adjacent parts of the frame and secondly by the

ulation of current round the frame perimeter. It was shown that the first of e supplemental effects (the radiation effect) and consequently the magnitude of resulting frame current depends on the ratio of the frame-dimensions to the e-length and on the angle of incidence of the wave upon the frame sides, the ction of propagation being in the plane of the frame—that is, on the shape and ntation of the frame; whilst the second supplemental, or current-distribution, ct depends only on the ratio of the frame-perimeter to the wave-length and is ependent of the shape and orientation of the frame.

A previous communication[2] dealt with this latter or current-distribution effect en not complicated by the former or radiation effect. The isolation of the two cts was accomplished by utilizing frames so shaped that they were deformatized* all angles of incidence with the particular wave-lengths in use. Furthermore it shown that the positions of the current nodes and antinodes were determined two currents circulating round the frame in opposite directions and that the ulting nodes and antinodes were fixed in space with reference to the position of transmitter.

The present paper deals with the radiation effect isolated from the current-tribution effect. It was thought that a study of the radiation effect by itself should nfirm the existence of those current-variations which have been anticipated[1] a result of revolving a short-wave rectangular frame aerial in its own plane.

§ 2. THEORETICAL CONSIDERATIONS

When a rectangular frame is formatized it is so shaped that the current at any nt in the frame becomes abnormally large compared with what it would be for rame of the same area but of arbitrary shape. The necessary conditions have en termed, for convenience, the "first formatizing conditions"[3]†. From them it lows that a square frame, if formatized when the wave-front is parallel to one side hen it is said to be in the "square position"), will become deformatized when the me revolves through 45° into the "diamond position", the current at any point coming less; and the reverse will occur if the frame be formatized for reception the diamond position.

First, we may consider what current-variations are to be expected if the easuring instrument moves round a fixed frame. The instrument will pass in ccession through the current nodes and antinodes spaced round the perimeter d so will record the current-distribution already discussed elsewhere[2]. If, wever, the instrument be fixed in the frame and both revolve together, then the served current-variations will differ from those recorded with a fixed frame. This ses because the instrument not only will pass in succession through the spacially ed current nodes and antinodes as before, but also will record current-variations

* That is, the ratios of the frame-dimensions to the wave-length were such that, at any given nt of the frame, the supplemental e.m.f. due to radiation from other parts of the frame did not gment or reinforce the initial e.m.f. due to a local oscillator or an incident wave. See reference (2), . 198, 199.

† See equations (1) below.

due to the fact that the frame may become alternately formatized and deformati as it revolves. For certain wave-lengths, current maxima due to this cause v occur whenever the frame is in the square position, whilst for other wave-leng maxima will occur when it is in the diamond position. Thus the current measu at any point will depend on the combination of the two different effects discus above.

The isolation of the radiation effect may be accomplished by measuring t current at any fixed point in space irrespective of the position of the point on t frame. The current at this point will vary with time as the revolving frame becom alternately formatized and deformatized, but it will not vary as a result of the n uniform current-distribution round the frame. This follows from the fact that t distribution is fixed in space and is dependent only on the position of the transmitt Consequently, if it can be so arranged that the current is always measured at t same point in space with respect to the transmitter, then any current-variati which may be recorded will be due to the fulfilment or non-fulfilment of the fi formatizing conditions as the frame revolves.

Thus, this method of using a current-measuring instrument fixed in sp enables the temporal current changes due to the first formatizing conditions to studied without any disturbing effect arising from the non-uniform spacial d tribution of the current round the frame.

It has already been shown* that the formatizing conditions arising from t mutual radiation between parallel limbs of a rectangular frame are given appro mately† by the odd solutions of the equations:

$$\left.\begin{aligned}\tan[a(1+\cos\gamma)-\psi] &= (a^2-1)/a \\ \tan[a'(1+\sin\gamma)+\psi] &= (a'^2-1)/a'\end{aligned}\right\} \quad \ldots\ldots(1).$$

W, a', H, λ where $a = 2\pi W/\lambda$, $a' = 2\pi H/\lambda$, W/λ and H/λ are the ratios of the frame-width a the frame-height respectively to the wave-length, γ the angle of incidence of t γ wave-front on the frame and ψ an arbitrary phase angle. ψ

The alternative solutions of these equations give the critical frame-dimensio for maximum and minimum current. The values of a and a' were found for vario values of ψ by a graphical method and curves were given showing the relati between W/λ and H/λ for different angles of incidence γ of the wave on the fra The first few curves for both maximum and minimum current conditions f $\gamma = 0°$ and $45°$ are given in figures 1 (a) and 1 (b) respectively. The critical wav lengths for a square frame, with which this paper is concerned, can be obtain from these curves by drawing a line through the origin at 45° to the axes and noti the values of W/λ (or H/λ) for the points where the straight line cuts the curves. this way the wave-lengths for both maximum and minimum current conditions c be deduced for a square frame in the square position ($\gamma = 0°$) or in the diamo position ($\gamma = 45°$).

We may now consider what current-variations are to be expected when a squa frame revolves in its own plane, the current being measured by an instrument whi

* Reference (1), p. 197.

† See preceding paper, p. 377 of this volume.

s always inserted in the frame at that point which is (say) nearest to the transmitter. For a wave-length for which the frame is always deformatized when at any angle to the wave-front, the current measured should show no temporal variation as the frame revolves. This conclusion has already been tested and the graph relating frame current to frame-angle was a straight line parallel to the frame-angle axis.*

Suppose now that the wave-length is changed so that the frame is formatized in the square position, that is, the ratio of the frame-sides to the wave-length is given by the coordinates of one of the points A, e.g. A_1 in figure 1 (*a*). Then when the frame is oriented so that one side is parallel to the wave-front, the current measured by an instrument inserted in the middle of the side nearest the transmitter will be a maximum because the frame will be formatized. As the frame revolves in either direction it becomes more and more deformatized, and the current (still measured by putting the ammeter at the fixed point nearest the transmitter) will decrease until the diamond position is reached when the current will be a minimum. Thus a graph relating frame current with frame-angle should no longer be a straight line parallel to the frame-angle axis but should show a current peak whenever the frame is in the square position, and this will occur four times in each revolution.

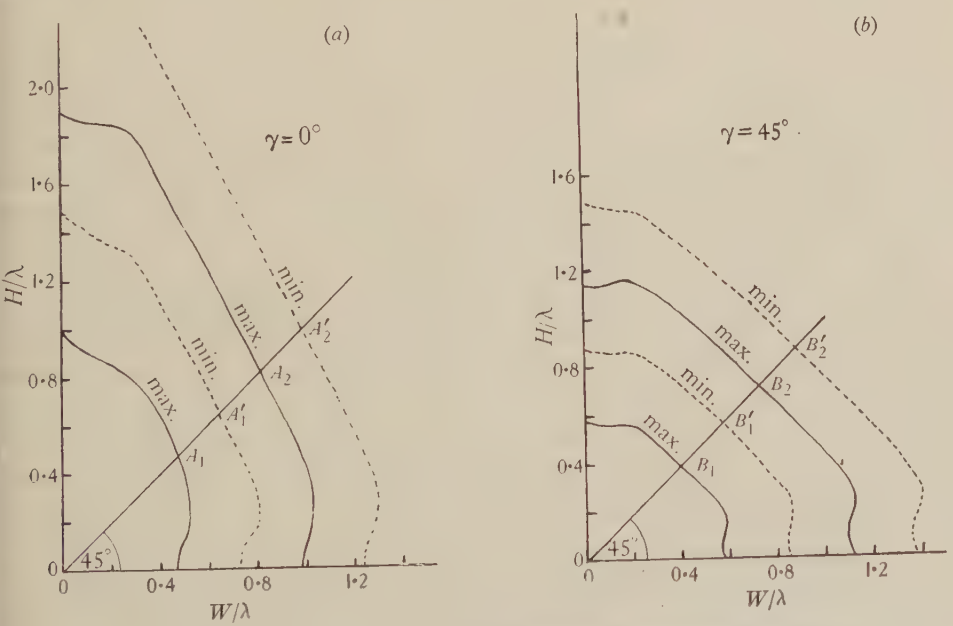

Figure 1. Graphical determination of theoretical formatizing dimensions for square receiving and transmitting frames.

By a precisely similar argument, when the wave-length is such that the frame is formatized in the diamond position, given by the coordinates of one of the points B, e.g. B_1 in figure 1 (*b*), then the graph relating frame current to frame-angle

* See reference (2), figure 10, and also the last diagram in figure 4 of this paper.

should show current-maxima whenever the frame is in the diamond position and current-minima whenever it is in the square position.

Consider now the case in which the wave-length is such that the frame is deformatized in the square position; this is given by the coordinates of one of the points A', e.g. A_1' in figure 1 (*a*). Then since the frame is not completely deformatized in the diamond position, which would occur at B_1' in figure 1 (*b*), a graph relating frame current to frame-angle should show a minimum in the square position and a maximum in the diamond position. Similarly, a current-maximum should be obtained when the frame is in the square position if the wave-length be such that the frame is deformatized in the diamond position. It is to be expected that these current variations will be repeated when the wave-length is progressively decreased so that the conditions indicated by the coordinates of the points B_2, A_2, B_2' and A_2' are successively fulfilled; and so on for the points B_n, A_n, B_n' and A_n' in general.

I_S, I_D

These theoretical deductions can best be shown on one graph by plotting against λ/W the logarithm of the ratio of the current I_S in the square position to that I_D in the diamond position. Positive peaks should then occur when the frame is formatized in the square position or deformatized in the diamond position, and negative peaks when it is formatized in the diamond position or deformatized in the square position.

§ 3. EXPERIMENTAL INVESTIGATION

Apparatus. The circuit of the short-wave transmitter used in these experiments was the ordinary series-fed Hartley circuit. To this was coupled a Hertzian dipole aerial of adjustable length, and in order to make the radiation as large and as uniform as possible the oscillator and coupling coil were screened with an iron box. An Osram D.E.T. 1.S.W. valve was employed. The wave-length range of the transmitter was from 5 to 12 metres.

Figure 1 (*a*) shows that, for a square frame to be formatized in the square position, the values of W/λ (or H/λ) must be either 0·47 or 0·82 (for points A_1 and A_2 respectively), whilst for the frame to be deformatized in the square position W/λ must be either 0·65 or 1·01 (for points A_1' and A_2' respectively). Similarly figure 1 (*b*) shows that for the square frame to be formatized in the diamond position W/λ must be either 0·39 or 0·72 (for points B_1 and B_2 respectively), and for it to be deformatized in the diamond position W/λ must be either 0·57 or 0·87 (for points B_1' and B_2' respectively).

As the wave-length range of the transmitter was limited, square receiving frames having sides of about 3 and 5 metres were used. With the smaller frame the minimum value of W/λ could be 3 12 or 0·25 whilst, with the larger frame, the maximum value of W/λ could be 5 5 or 1·0. In this way all the critical values deduced above from figure 1 could be studied.

One method of keeping the current measuring-instrument fixed in space as the frame revolved was as follows. The aerial wire of the frame was passed round insulated pulleys on the four corners of a suitable wooden framework which could rotate on a horizontal axis secured at a little distance from the top of a 40-foot

scaffold pole. The current was measured by a vacuum thermojunction. Where the thermojunction was inserted in the frame, the aerial wire was shunted by a condenser of 0·0005-μF. capacity which tuned that portion of the frame to the wavelength in use. The current in the shunted portion of the aerial wire varied in the same way as that in the adjacent parts of the frame but was of greater magnitude and consequently easier to measure. The thermojunction was connected by a short length of flex to a microammeter which rested on a small platform hanging from a pivot clamped to the framework. The condenser, thermojunction and microammeter could be moved along one side of the frame and could be clamped in any required position.

The height of the frame above the ground was such that any change in its capacity to earth due to its revolving was negligibly small. The transmitter with a horizontal radiating dipole was placed vertically below the frame, so that if waves reflected from the ground affected the frame they were incident at the same angle as the waves arriving directly from the transmitter. The microammeter was read from the ground by means of a telescope and mirror because an observer near the frame would distort the field.

A second method of obtaining the desired current-measurements was to duplicate the thermojunction, microammeter and condenser. One thermojunction connected to a microammeter and a condenser was fixed in the middle of one of the frame sides, and another identical thermojunction, also connected to a microammeter and a condenser, was fixed at one corner of the frame. The whole frame with its two fixed instruments could revolve from the square to the diamond position and that instrument was read which was occupying the particular point in space at which the current was to be measured. In this way the ratio of the current when the frame was in the square position to the current when the frame was in the diamond position could be determined for a series of different wave-lengths.

Some of the observations were made with the frames in the horizontal plane about five feet above the ground and rotating about a vertical axis.

Current-measurements. It is convenient to consider the current-measurements under two sub-headings: (i) current-variations with a fixed frame, the instrument moving round the frame perimeter; and (ii) current-variations with a revolving frame, the instrument fixed in space relative to the transmitter.

(i) Frame fixed: instrument moving round frame. Experiments with the instrument moving round a fixed frame were carried out to test the form of the current-distribution round the frame when the latter was formatized and deformatized in both the square and the diamond positions. As an example the results with a frame 3·06 metres square are shown in figures 2 and 3 for wave-lengths of 6·52 and 7·89 metres respectively. For these wave-lengths W/λ is 0·47 and 0·39 respectively and hence the frame is formatized in the square positions and deformatized in the diamond positions for the case shown in figure 2, whilst it is deformatized in the square positions and formatized in the diamond positions for the case shown in figure 3. These results are discussed in § 4 below.

(ii) Frame revolving: instrument fixed in space. In the series of experiments with one measuring-instrument in the frame the procedure was as follows. The frame was turned to the diamond position and the instrument was placed at the corner of the frame nearest the transmitter. After the observation had been made through the telescope, the instrument was moved a short distance along the frame

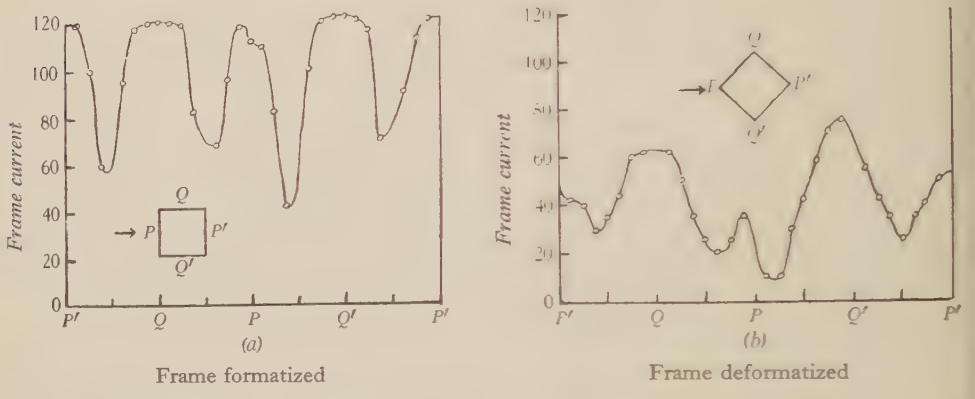

Figure 2. Current-distribution round a fixed frame with side measuring 3·06 m. Wave-length, 6·52 m.

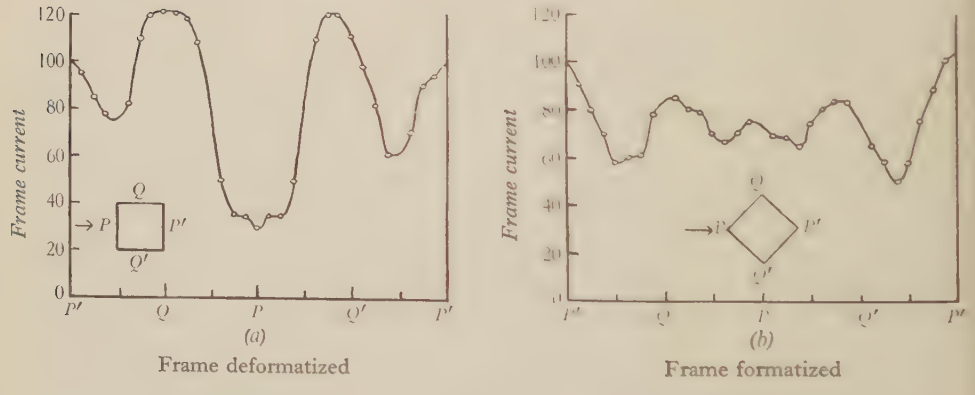

Figure 3. Current-distribution round a fixed frame with side measuring 3·06 m. Wave-length, 7·89 m.

which was then revolved until the instrument came back to the same position in relation to the transmitter. The aerial wire moved round the insulated pulleys at the corners of the framework as the thermojunction etc., to which the ends of the aerial wire were attached, moved along the side of the frame.

In this way the frame was turned from one diamond position through a square position to the next diamond position. This procedure was adopted in the case of the 3-metre frame for wave-lengths varying from 5 to 12 metres, and for the

5-metre frame for wave-lengths varying from 5 to 10 metres. Some of the results are shown in the series of separate diagrams arranged in figures 4 and 5.

In the case of the frame with two fixed thermojunctions, the current measurements could only be taken when the frame was in the square or the diamond position. This was necessarily so because only when the frame was turned into one of those two positions was a thermojunction brought into that particular point in space at which the current was being measured. In the case of these experiments

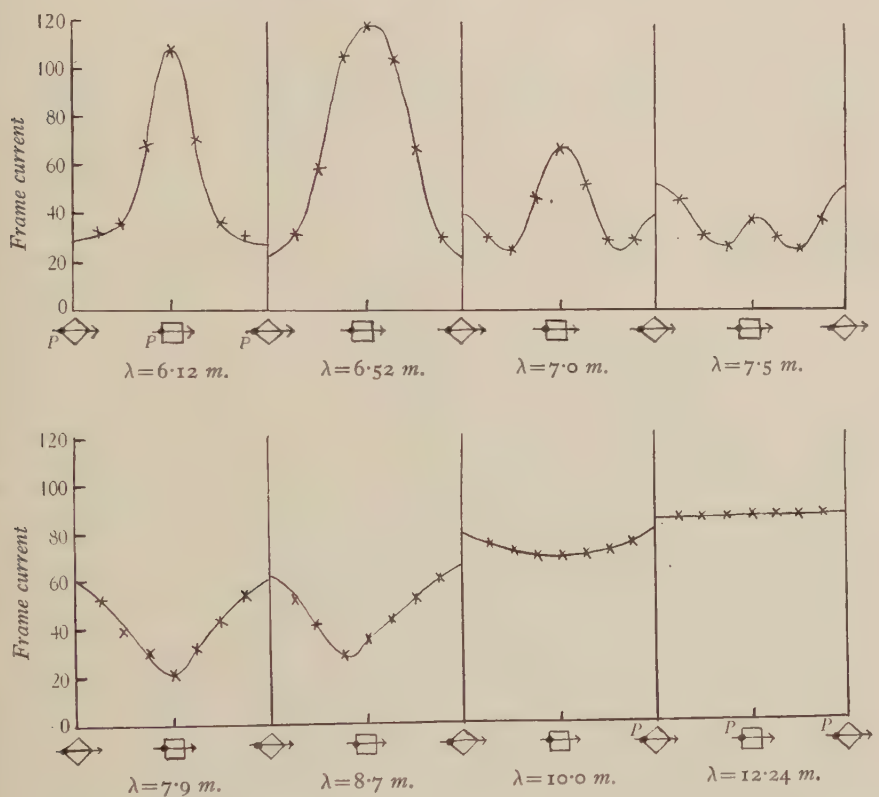

Figure 4. Current-measurements at P with frame revolving and instrument fixed. Frame 3·06 metres square.

that particular point in space was the point of the frame nearest to the transmitter (points P on the inset diagrams of figures 2 and 3). The results of these experiments are plotted as circles in figure 6, in which the gain in the current I_S when the frame was in the square position over that I_D when the frame was in the diamond position is expressed in decibels. The reference letters on this figure correspond with those in figures 1 (*a*) and (*b*).

All these results will now be considered in the light of the theoretical conclusions of § 2 above.

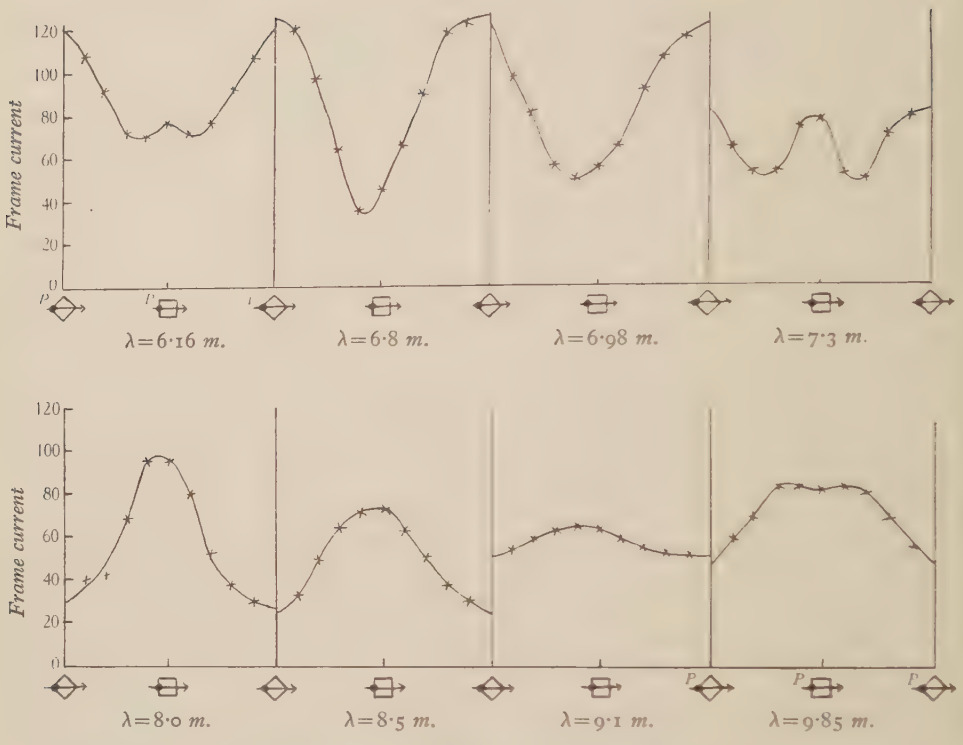

Figure 5. Current-measurements at P with frame revolving and instrument fixed. Frame 4·93 metres square.

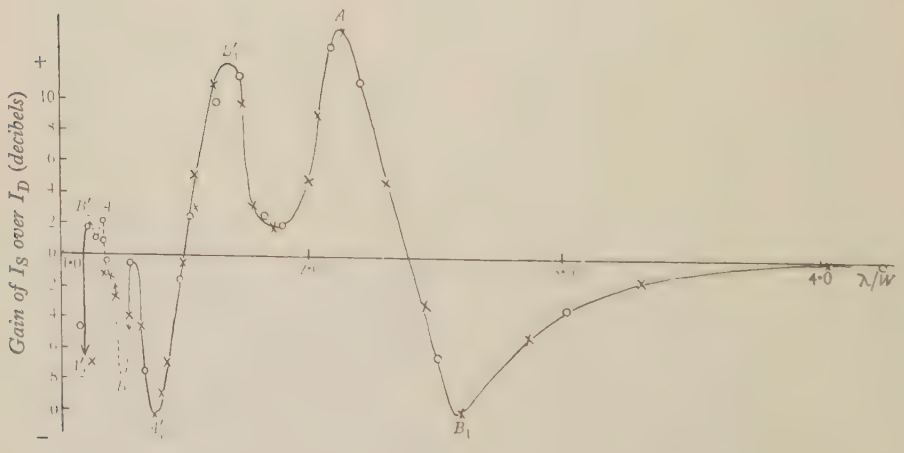

Figure 6. Variation of current-ratio with wave-length as a square frame revolves from the square to the diamond position.

§ 4. DISCUSSION OF RESULTS

From figures 2 and 3, which show the current-distribution round a fixed frame, the first conclusion that is evident is the one previously obtained; namely, the fixity of the current nodes and antinodes in space and their complete independence of the orientation of the frame with respect to the wave-front and to the position of the thermojunction and condenser.

The second conclusion arises from a comparative study of the temporal variation of the current at the fixed point P. This is the main objective of this paper. In figure 2 the current at this point has *decreased* as the frame turned from the square to the diamond position and so became deformatized, W/λ being 0·47 and not 0·39. The reverse has taken place with the current at P in figure 3. Here the current *increased* as the frame revolved to the diamond position, but W/λ now equals 0·39 for which ratio the frame is formatized in the diamond position.

Although these conclusions also apply to the other current antinodes in figure 2, they are not applicable to the antinodes at Q and Q' in figure 3. This is referred to again below in connection with figure 6.

Let us now turn to figures 4 and 5, which depict the current-variations at the fixed point P as the frame revolves. In figure 4 it is seen that there is a gradual transition throughout the range of wave-lengths used. Starting at 6·12 metres the variation due to formatizing is clearly indicated by the current peak when the frame is in the square position, and this becomes more pronounced when the wave-length is increased to 6·52 metres and the difference between the currents in the square and diamond positions is greatest. That is, the frame is formatized in the square position for a wave-length of 6·52 metres; this corresponds to point A_1, figure 1. Between 6·52 metres and 7·9 metres a transition occurs, and at about 7·9 metres the frame is formatized in the diamond position; this corresponds to point B_1 in figure 1. For wave-lengths longer than 7·9 the difference between the currents when the frame is in the square and diamond positions becomes less until at about 12 metres the current is sensibly constant, showing that there is no formatizing effect.* In order to illustrate in one diagram these progressive changes arising from points A_1 and B_1 in figure 1, and also the changes recorded in figure 5 which arise from points A_1' and B_1' in figure 1, together with other similar results not here figured, the ratio of the current I_S when the frame was in the square position to the current I_D when it was in the diamond position has been expressed in decibels, and the resultant values are marked as crosses in figure 6. With reference now to figure 6, it has been shown on page 392 that peaks should occur when the frame was either formatized in the square position (points A) or deformatized in the diamond position (points B') and troughs should occur when the frame was either formatized in the diamond position (points B) or deformatized in the square position (points A'). In the table on p. 398 the theoretical positions of these peaks (+) and troughs (−) are taken from figures 1 (*a*) and 1 (*b*) and are compared with the experimental values from figure 6.

* Cf. figure 10 on page 84 of reference (2).

A portion of the graph is shown dotted because, in order to obtain sufficient experimental values to fix the exact position of the curve, the change in λ / W had to be of the order of one per cent and this could not be controlled to the required degree of accuracy with the apparatus available. Nevertheless a slight change in wave-length showed at once whether any two adjacent points were on a portion of the curve with a positive or with a negative slope. Thus it is certain that where the value of λ/W is in the neighbourhood of 1·3 there are two troughs and not one, and where it is about 1·15 there are similarly two peaks.

Critical values of λ/W								
Reference letter	B_1	A_1	B_1'	A_1'	B_2	A_2	B_2'	A_2'
Theoretical values from figure 1	−2·56	+2·12	+1·75	−1·54	−1·39	+1·22	+1·15	−0·99
Experimental values from figure 6	−2·58	+2·13	+1·69	−1·38	−1·25 (?)	+1·17 (?)	+1·11 (?)	−?

Hence it is thought that, in spite of the difficulties of these short-wave experiments, the agreement between the number and order of the peaks and troughs as determined by experiment and as deduced from figure 1 tends to support the theory of formatization upon which the graphs of figure 1 are based. This agreement is perhaps all the more interesting when it is realized that with the shorter wave-lengths there may be at least two current antinodes along any one limb of the frame, the current at any instant being in opposite phases at adjacent antinodes.

In conclusion it may be asked whether the current-increase which occurs when the frame becomes formatized is due to a decrease in the apparent impedance of the whole frame, or to a redistribution of a constant total current between the several current-antinodes. Figure 2 suggests that the whole frame has a reduced impedance when it is formatized, whilst figure 3 seems to support the second suggestion, since the current at Q and Q' seems to have decreased when the frame became formatized. Other experiments now in progress indicate that probably both these factors are involved.

Of the practical consequences of the foregoing work, two are immediately evident. (i) It depends on the wave-length whether it is best to orient a given square frame aerial in the square or in the diamond position, and (ii) a current-actuated or voltage-actuated instrument will function best when placed at certain specific points round the frame.

We may now summarize the results of this investigation by the following statement. *When a short-wave square frame aerial revolves in its own plane, then in addition to spatial current variations round the perimeter due to the formation of fixed current nodes and antinodes, there may also be temporal current variations at any fixed point due to the fact that the frame may become alternately formatized and deformatized as it revolves.*

§ 5. ACKNOWLEDGMENT

We should like to record our thanks to Mr Watson Watt who kindly loaned the short-wave transmitter, and also to Mr Denis Taylor for assistance in carrying out the experiments.

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RAPID MATHEMATICAL METHODS FOR TRICHROMATIC COLORIMETRY

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ABSTRACT. Methods are suggested for reducing the labour involved in colorimetric transformations, with particular application to routine industrial measurements. The calibration of an instrument by measurement of illuminant *B* is replaced by measurement of a suitable stable filter and the illuminant in usual use. A nomographic method of conversion from instrument readings to the C.I.E. basis is suggested, and a graphical method is given for conversion to terms of hue and saturation. Scales are given for a graphical method of converting from the spectrophotometric curve of a coloured specimen to the trichromatic coefficients with a series of illuminants on the C.I.E. basis. The errors of these methods are estimated for comparison with the errors of observation on a Hilger-Guild trichromatic colorimeter.

§ 1. INTRODUCTION

THE majority of those who have investigated the use of a system of trichromatic colorimetry have developed some arithmetical or graphical method of simplifying the mathematics of the transformation with which they have been concerned. This has become increasingly necessary within the last fifteen years, owing to the continued use of different systems of primaries and to the need of coordination of the trichromatic system with the monochromatic-plus-white system. The basic principles of several transformations were given in two papers by Ives[1] and were followed by arithmetical applications by Froelich[2] in America and by Guild[3] in this country. Geometric methods and a variety of arithmetical methods have been derived since. The majority of these methods are arithmetically accurate; it is the purpose of this paper to put forward both graphical and observational methods of a sufficiently high order of accuracy for industrial or routine measurements, and for guidance in cases where the extreme accuracy required in the standardization of instruments or the designation of standard colours is not required. An accuracy of 1 per cent is all that can usually be expected in industrial colorimetry, and a mathematical tolerance of $\frac{1}{10}$ of this amount allows of compromises which effect a considerable acceleration of the calculations involved in some of these transformations.

§ 2. OBSERVATIONAL ERROR

The most recent measurements[4, 5] of the hue limen of fully saturated colours and of the saturation limen throughout the spectrum indicate that differences of hue of less than 2·0mμ., and that differences of saturation of less than 5 per cent,

annot be discerned in a single observation, except in certain limited areas of the olour triangle. For routine measurements, sufficient accuracy is assured if the ross probable error of the observational method is definitely less than the liminal olerance at that point.

The errors of the method comprise the instrumental inaccuracies, the errors of eading the scales, and the errors of the transformation from scale readings to bsolute values. The first of these may be sub-divided into mechanical inaccuracies hich will be negligible in all well-designed instruments, and the inaccuracies troduced by irregular variation of the source of light and of the components of he optical system. These latter errors are extremely difficult to estimate but pre-autions may be taken to reduce their effect. The errors of reading depend on the ccuracy and clarity of the scales, which again can usually be made fairly satis-ctory. The errors of the transformations are the subject of this discussion.

Besides the errors inherent in the method there are the errors in the setting of he colorimeter, and an attempt has been made to estimate the error which obtains n the use of the Hilger-Guild trichromatic colorimeter. Statistical treatment has een applied to thirty-four routine measurements of illuminant *B* by two normal bservers, the measurements being spread over several weeks and carried out with ifferent solutions and different arrangements of the auxiliary apparatus. Each neasurement was the mean of two settings taken with both the colorimeter lamp nd the standard lamp maintained at steady potentials, and the readings of the hree sectors on the instrument were reduced to unit sum for the purpose of com-arison. The coefficients of variation for each observer were as shown in table 1.

Table 1. Observers' coefficients of variation (per cent)

Observer	Red sector	Green sector	Blue sector	Mean
A. H. A.	1·15	1·76	0·90	1·27
J. G. H.	1·10	1·25	0·66	0·99
Mean	1·12	1·50	0·78	1·13

The procedure which the author has adopted is that two settings are made on ach specimen and the mean, obtained by mental arithmetic, is written down. This taken as sufficiently reliable for most commercial purposes, but if greater ccuracy is required the whole series of observations is repeated by the same ethod until the reliability of the results is ensured.

§ 3. ROUTINE CALIBRATION OF INSTRUMENT AND OBSERVER

The method to be employed for the calibration of the Hilger-Guild instrument that in which a match is made on illuminant *B* and subsequent readings on any olour are divided by the sector readings of this match, so that the unit equation f illuminant *B* is $1/3R+1/3G+1/3B$. If the colorimeter is regularly used with an luminant operated at 2360° K., as for signal glassware, or with illuminant *A*, as

for lighting fittings, it is convenient to eliminate the preliminary setting on illuminant *B*, and this may be done by making a setting on the illuminant in use and applying a correction during the transformation of subsequent readings. Two methods are available for this.

It is frequently of value to know the unit equations of the standard illuminants in terms of the instrumental system. The original calibration of the instrument by spectrophotometric measurement of the filters gives the colour equations, in terms of the C.I.E. basis, of the unitary stimuli corrected for intensity, so that illuminant *B* is matched by numerically equal proportions of each, and these equations may be applied to transform the accepted C.I.E. colour equations of the illuminants to the instrumental basis. For the particular colorimeter which the author is considering the equations are as shown in table 2.

Table 2. Calibration equations for Hilger-Guild colorimeter No. H93304 27206

Instrumental stimuli	$R = 0{\cdot}744X + 0{\cdot}288Y + 0{\cdot}000Z$ $G = 0{\cdot}151X + 0{\cdot}721Y + 0{\cdot}075Z$ $B = 0{\cdot}150X + 0{\cdot}046Y + 0{\cdot}825Z$
Illuminant *A*	$Q_A = 0{\cdot}4476X + 0{\cdot}4074Y + 0{\cdot}1450Z$ $= 0{\cdot}501R + 0{\cdot}356G + 0{\cdot}143B$
Illuminant *B*	$Q_B = 0{\cdot}3484X + 0{\cdot}3516Y + 0{\cdot}3000Z$ $= 0{\cdot}333R + 0{\cdot}333G + 0{\cdot}333B$
Illuminant *C*	$Q_C = 0{\cdot}3100X + 0{\cdot}3162Y + 0{\cdot}3738Z$ $= 0{\cdot}269R - 0{\cdot}305G - 0{\cdot}426B$
Equi-energy white	$Q_E = 0{\cdot}3333X + 0{\cdot}3333Y + 0{\cdot}3333Z$ $= 0{\cdot}309R + 0{\cdot}315G + 0{\cdot}376B$
2360° K.	$Q_{2360^\circ} = 0{\cdot}4894X + 0{\cdot}4150Y + 0{\cdot}0956Z$ $= 0{\cdot}575R + 0{\cdot}340G + 0{\cdot}085B$
1900° K.	$Q_{1900^\circ} = 0{\cdot}5372X + 0{\cdot}4114Y + 0{\cdot}0514Z$ $= 0{\cdot}657R + 0{\cdot}309G + 0{\cdot}034B$

If a match is made on one of these illuminants and the sector readings are divided by factors chosen to yield the appropriate unit equation on the instrumental system, the same factors can be applied to subsequent sector readings to reduce the results for all colours to the instrumental system. This method of eliminating illuminant *B* is not of high accuracy in the blue when used with a source at 2360 K. A higher accuracy is obtainable by using a glass or stable gelatine filter which when combined with the usual illuminant, gives a colour similar to that of illuminant *B*, which is itself a combination of a liquid filter and illuminant *A*. This gives a calibration as accurate as illuminant *B* itself would give, and has the advantage that the instrument may be calibrated without the use of fresh solutions in the Davis-Gibson filter or without any doubts as to the freshness of the solutions. It is advisable to have the spectrophotometric curve of the glass filter determined accurately and to calculate the equation of the colour which it gives with the illuminant with which it is most used. When a match is made on this combination the factors necessary to reduce the sector readings to the unit equation of the

colour can be used for a conversion of subsequent sector-readings. For example, a particular glass of the ordinary half-watt-to-daylight type, when used with illuminant A, gives an equation as follows:

$$Q_D = 0{\cdot}270R + 0{\cdot}378G + 0{\cdot}352B. \qquad Q_D$$

This glass has been used consistently without any apparent error in the author's colorimeter. It is possible to select other blue glasses which would give a closer approximation to illuminant B with either 2360° K. or illuminant A.

§ 4. CONVERSION FROM THE INSTRUMENTAL SYSTEM TO C.I.E. SYSTEM

The coefficients of the colour equation of any particular specimen on the instrumental system may be converted to the C.I.E. system by replacing the instrumental stimuli, as they appear in the equation, by their own equations on the C.I.E. system, which will have been obtained in the original calibration of the instrument.

The arithmetical transformation is easy, but a nomographical method is available which converts the unit equation on the instrumental system to an equation on the C.I.E. system, the sum of whose coefficients is sufficiently close to unity to enable the unit equation to be written down by the aid of a slide rule. A nomogram made on the principles outlined below, on a card measuring 20 in. by 30 in., gives figures reliable to 0·001 in the unit equation.

Suppose the colour to be represented by

$$C = r.R + g.G + b.B, \qquad r, g, b$$

where r, g, b are known, and

$$r + g + b = 1.$$

The original calibration of the colorimeter would yield equations of the form

$$R = \rho_1.X + \rho_2.Y + \rho_3.Z, \qquad \rho$$

$$G = \gamma_1.X + \gamma_2.Y + \gamma_3.Z, \qquad \gamma$$

$$B = \beta_1.X + \beta_2.Y + \beta_3.Z. \qquad \beta$$

The required equation is then

$$C = x.X + y.Y + z.Z,$$

where

$$x = r.(\rho_1 - \gamma_1) + \gamma_1 + b.(\beta_1 - \gamma_1), \qquad x$$

$$y = r.(\rho_2 - \gamma_2) + \gamma_2 + b.(\beta_2 - \gamma_2), \qquad y$$

$$z = r.(\rho_3 - \gamma_3) + \gamma_3 + b.(\beta_3 - \gamma_3). \qquad z$$

In a nomogram of the form shown in figure 1 the R, G and B scales will be at equal separation, the G scale being reversed and with half the unit of the R and B scales, so that $r - g + b = 1$. If the total separation of the R and B scales is D, and D

d the unit of these scales is d, the positions and units of the X, Y and Z scales can be shown to be as follows:

Position of X scale ... $\dfrac{(\beta_1-\gamma_1).D}{\rho_1+\beta_1-2\gamma_1}$ from R scale.

Position of zero on X scale $-\gamma_1$.

Unit distance on X scale $d/(\rho_1+\beta_1-2\gamma_1)$.

Position of Y scale ... $\dfrac{(\beta_2-\gamma_2).D}{\rho_2+\beta_2-2\gamma_2}$ from R scale.

Position of zero on Y scale $-\gamma_2$.

Unit distance on Y scale $d/(\rho_2+\beta_2-2\gamma_2)$.

Position of Z scale ... $\dfrac{(\beta_3-\gamma_3).D}{\rho_3+\beta_3-2\gamma_3}$ from R scale.

Position of zero on Z scale $-\gamma_3$.

Unit distance on Z scale $d/(\rho_3+\beta_3-2\gamma_3)$.

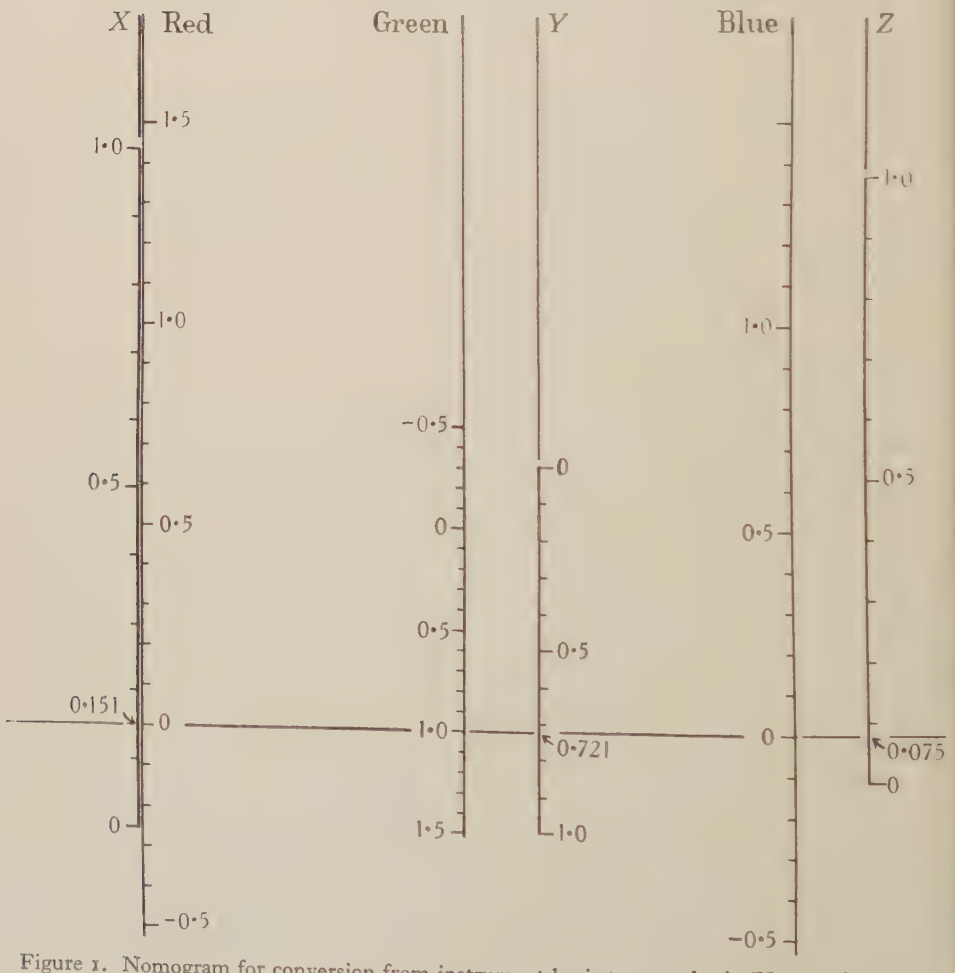

Figure 1. Nomogram for conversion from instrument basis to C.I.E. basis (H 93304/27206).

The nomogram shown is for the Hilger-Guild colorimeter, whose calibration uations are given in table 2.

As an instance of the use of this nomogram, consider the conversion of the our equation of a half-watt-to-daylight glass, with illuminant A, from the trumental basis to the C.I.E. basis. The unit equation on the former basis is

$$Q_D = 0{\cdot}270R + 0{\cdot}378G + 0{\cdot}352B.$$

If a straight line, such as a stretched steel wire, be placed across the diagram rough the points $0{\cdot}270R$ and $0{\cdot}352B$, it will also be found to pass through the int $0{\cdot}378G$, and so this line now represents the equation of the colour. This e will be found to intersect the X, Y and Z scales at the points $0{\cdot}311X$, $0{\cdot}366Y$ d $0{\cdot}318Z$. The sum of these coefficients is 0·995 and the unit equation may be itten down at once:

$$Q_D = 0{\cdot}312X + 0{\cdot}368Y + 0{\cdot}320Z.$$

These coefficients are the same as those found by the arithmetical transformation. ne same process may be applied if some of the coefficients of R, G and B in the it equation are negative or greater than unity. The sum of the values of X, Y d Z given by the intersections will always be close to unity, so the evaluation of e unit equation on the C.I.E. basis is a matter of mental arithmetic or a simple de-rule conversion.

§ 5. COLORIMETRIC SATURATION

The specification of a colour in terms of the coefficients of the three unitary muli X, Y and Z is a complete description which is internationally comparable, t it is not generally possible to visualize the colour immediately from those ures, and although the specification is undoubtedly the best for all records or act statements, there is a use for the conception of hue and saturation as a means describing a colour. This latter method is liable to much abuse, for it can only exact when care is taken to specify the white light which is taken as the reference int of the hue and saturation, and different sets of figures are not comparable less the same white diluent is used for each.

The method is based on the experimental fact that any colour may be matched the combination of two stimuli in suitable proportion, provided that the three ints given by plotting their trichromatic coefficients on a linear scale are collinear. general, the two stimuli chosen are the equi-energy white, which is termed the luent, and a spectral colour, which is termed the hue wave-length. The colori-etric saturation is then the percentage of the spectral component when both imuli are measured in units of the same luminosity.

The transformation from the trichromatic system to the homogeneous-plus-terogeneous system may be performed in various ways. Two exact methods have en proposed, one by Smith and Guild[6] and one by Judd[7], both of which are sisted if a plot of the spectrum locus is used. In practice the system is not used nder conditions where exact specification is necessary, and an approximate trans-rmation can be read off a graph if loci of equal saturation are plotted inside the

spectrum locus. It is obvious that these loci will only apply to one particular whit diluent, but as it is not the general practice to use anything but equi-energy whit for this purpose, the iso-saturation loci with reference to equi-energy white may b calculated with advantage.

Taking the general case, let us define the following stimuli on some trichromati system:

R, G, B	Coefficients of heterogeneous stimulus (white diluent)	R, G, B.
r', g', b'	Coefficients of homogeneous stimulus (hue wave-length or spectral component)	r', g', b'.
r, g, b	Coefficients of combined colour of above, in specified proportions	r, g, b.
L_w, L_λ, L_c	Luminosities of above stimuli, respectively ...	L_w, L_λ, L_c.
L_r, L_g, L_b	Luminosities of unitary stimuli of system ...	L_r, L_g, L_b.
σ	Saturation of combined colour	σ.

One luminous unit of the combined colour is proportional to the reciprocal o its luminosity:

$$\frac{1}{L_c} = \frac{1}{r.L_r + g.L_g + b.L_b} \qquad \text{.....(1).}$$

Also, by definition of "saturation",

$$\frac{1}{L_c} = \frac{\sigma}{L_\lambda} + \frac{1-\sigma}{L_w} \qquad \text{.....(2).}$$

Because the three points are collinear:

$$\frac{r-R}{r'-R} = \frac{g-G}{g'-G} = \frac{b-B}{b'-B} = \delta,$$

or $$r = R + \delta\,(r'-R), \text{ etc.}$$

After insertion of these in equation (1),

$$\frac{1}{L_c} = \frac{1}{L_w + \delta\,(L_\lambda - L_w)} \qquad \text{.....(3).}$$

Then, from equations (2) and (3),

$$\frac{1}{\delta} = 1 + \frac{L_\lambda}{L_w}\left(\frac{1}{\sigma} - 1\right).$$

Let the linear distance from the diluent to the hue wave-length on a char such as figure 2 be d_λ, and let the distance from the diluent to the combined colou be d_σ.

d_λ
d_σ

Then

$$\frac{d_\sigma}{d_\lambda} = \frac{r'-R}{r-R}$$

$$= \frac{1}{\delta}$$

$$= 1 + \left(\frac{1}{\sigma} - 1\right)\frac{r'.L_r + g'.L_g + b'.L_b}{R.L_r + G.L_g + B.L_b} \qquad \text{.....(4).}$$

The final equation gives the ratio of the distances on the colour chart between ints corresponding to the diluent, the spectral component and the combined

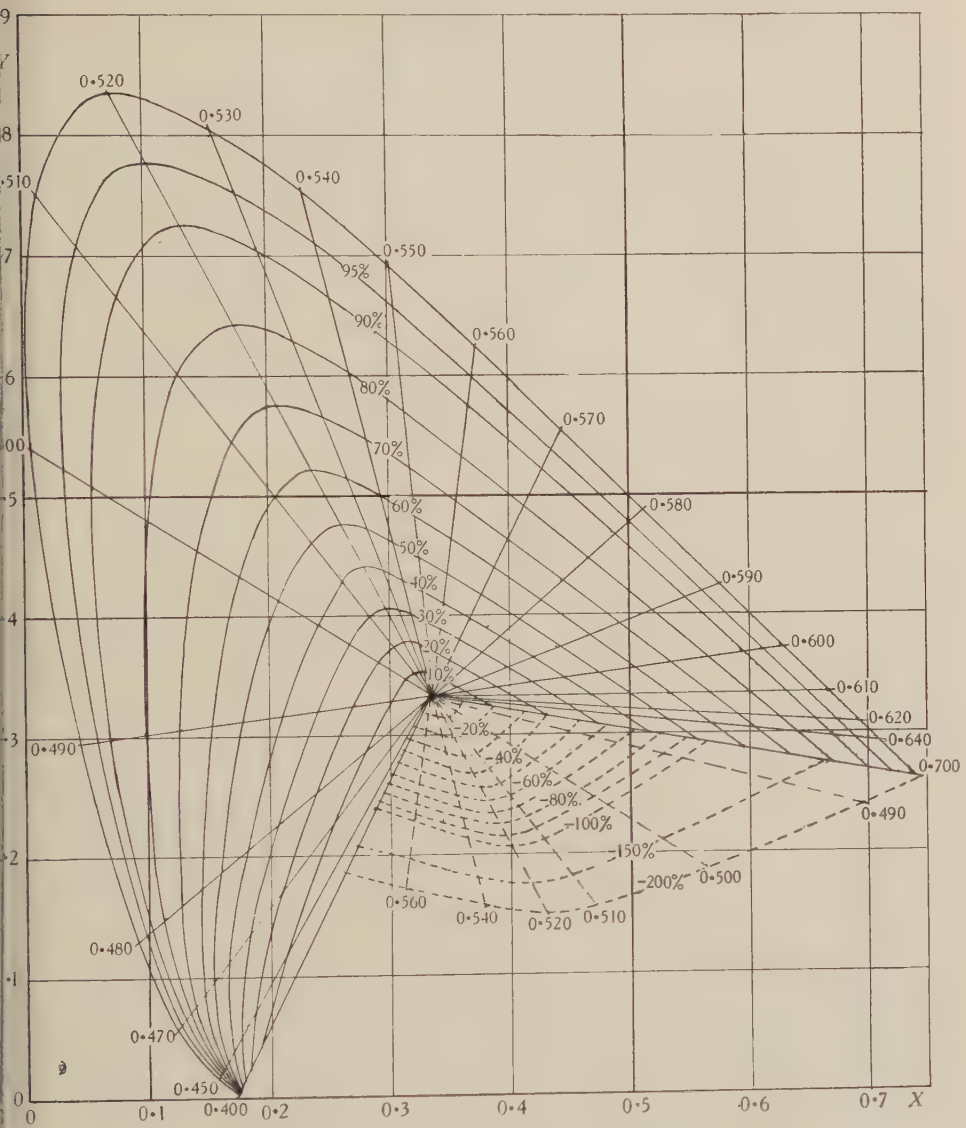

Figure 2. Iso-saturation loci on C.I.E. basis.

olour, in terms of the known constants of the system. Reducing this to the C.I.E. stem, we have

$$\frac{d_\sigma}{d_\lambda} = 1 + \left(\frac{1}{\sigma} - 1\right) \cdot 3y,$$

hich is the same as the equation obtained in Smith and Guild's method.

The use of the distances of the points on the chart from the diluent permits of

a rapid calculation of the iso-saturation loci, and the curves shown in figure 2 were obtained by this method. From these curves, tables may be compiled for permanent record, but the results are best used in their diagrammatic form.

If frequent use is to be made of a chart of this type in conjunction with a particular colorimeter, the figures can be calculated on the instrumental system by means of the relation given as equation (4) with equi-energy white as diluent and the results are then directly converted from the unit equation on the instrumental basis to terms of the hue and saturation with reference to equi-energy white without the intermediate step of the C.I.E. system. The more exact algebraic transformations derived by Smith and Guild and by Judd may equally well be applied to the instrumental basis if necessary, by an extension of the same reasoning.

It should be noted that if a chart of the type shown in figure 2 is employed for transformation from one system to the other it should be drawn on a card approximately 24 inches square or larger in order to ensure an accuracy of one figure in the third decimal place. If this is not practicable or convenient, sections of the chart, which need not necessarily include the centre, can be used with equal facility.

§ 6. TRANSFORMATION FROM SPECTROPHOTOMETRIC DATA TO TRICHROMATIC COEFFICIENTS

The simple algebraic method of making this transformation is to multiply the brightness factor at each of a series of wave-lengths by the corresponding figures $E\bar{x}$, Ey and $E\bar{z}$ given in the computational table of the illuminant. This latter figure is the product of the energy E of the source at that wave-length and the distribution coefficients $\bar{x}$, y and $\bar{z}$ for the equi-energy stimulus, which are actually the product of the standard visibility function V and the trichromatic coefficients x, y and z, divided by the coefficient y, which is a measure of the luminosity at that wave-length. The computational tables for standard illuminants A, B and C[9] and for 1900° K.[8] have already been published together with illustrative calculations and table 3 gives the computational data for a source at 2360° K., carried to the third decimal place.

$E\bar{x}$, Ey, $E\bar{z}$
E
$\bar{x}$, y, $\bar{z}$

A graphical method of making this transformation is available. Difficulties of accurate planimetry limit its accuracy to ± 0·5 per cent, but it effects a considerable saving of time when there are several results to be converted. The method consists of integrating the areas below the curves in which the spectrophotometric brightness factor is the ordinate and the wave-lengths, spaced according to the values of Ex, Ey and $E\bar{z}$, are the abscissae.

A different wave-length scale will be required for each unitary stimulus and for each illuminant, but when once the charts have been prepared on stiff paper they may be used almost indefinitely. The spacing of the wave-length scales is such that the intervals are proportional to the value of Ex, Ey or $E\bar{z}$ at corresponding wave-lengths and table 4 gives the scales for the standard illuminants A, B and C and for Planckian sources at 2360° K. and 1900° K. on a basis of a 10-in. scale for the coefficient of Y, giving points at every 10mμ.

The integrated visible-brightness factor of the specimen is given by the value which the coefficient of Y has before reduction to the unit equation has taken place.

§ 7. ACKNOWLEDGMENT

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Table 3. Computational data for 2360° K. illuminant (C_2=14,350 micron-degrees)

Wave-length (mμ.)	Relative energy distribution	$E\bar{x}$	$E\bar{y}$	$E\bar{z}$
380	0·38708	0·001	0·000	0·002
390	0·51039	0·002	0·000	0·010
400	0·66420	0·009	0·000	0·042
410	0·85016	0·035	0·001	0·165
420	1·0485	0·132	0·004	0·635
430	1·3355	0·355	0·015	1·735
440	1·6427	0·537	0·035	2·694
450	1·9950	0·630	0·071	3·316
460	2·3977	0·654	0·135	3·762
470	2·8530	0·523	0·243	3·442
480	3·3620	0·302	0·438	2·564
490	3·9283	0·118	0·766	1·713
500	4·5504	0·021	1·379	1·161
510	5·2318	0·046	2·469	0·776
520	5·9704	0·355	3·974	0·438
530	6·7671	1·051	5·472	0·268
540	7·6234	2·078	6·820	0·145
550	8·5349	3·471	7·964	0·070
560	9·5028	5·300	8·864	0·035
570	10·521	7·521	9·410	0·021
580	11·594	9·962	9·465	0·018
590	12·713	12·245	9·024	0·013
600	13·879	13·840	8·218	0·010
610	15·085	14·200	7·122	0·004
620	16·336	13·092	5·845	0·003
630	17·620	10·615	4·381	0·000
640	18·937	7·962	3·110	0·000
650	20·279	5·395	2·035	0·000
660	21·652	3·348	1·239	0·000
670	23·044	1·890	0·692	0·000
680	24·454	1·074	0·391	0·000
690	25·879	0·551	0·199	0·000
700	27·309	0·292	0·105	0·000
710	28·754	0·156	0·057	0·000
720	30·182	0·082	0·028	0·000
730	31·645	0·041	0·015	0·000
740	33·079	0·022	0·009	0·000
750	34·522	0·010	0·003	0·000
760	35·851	0·007	0·002	0·000
770	37·357	0·000	0·000	0·000
780	38·748	0·000	0·000	0·000
		117·925	100·000	23·042

$$Q_{2360°\,K.} = 0{\cdot}4894X + 0{\cdot}4150Y + 0{\cdot}0956Z.$$

Table 4. Abscissae for standard illuminants

Wavelength (mμ.)	Illuminant *A*			Illuminant *B*			Illuminant *C*		
	X	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*
380	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·001
390	0·000	0·000	0·001	0·001	0·000	0·004	0·001	0·000	0·003
400	0·001	0·000	0·006	0·004	0·000	0·018	0·005	0·000	0·027
410	0·005	0·000	0·026	0·016	0·000	0·075	0·024	0·001	0·113
420	0·021	0·001	0·099	0·063	0·002	0·301	0·095	0·003	0·457
430	0·066	0·002	0·319	0·202	0·007	0·980	0·318	0·010	1·488
440	0·146	0·006	0·705	0·441	0·020	2·158	0·664	0·029	3·249
450	0·245	0·015	1·222	0·716	0·044	3·568	1·063	0·064	5·298
460	0·348	0·031	1·790	0·978	0·084	5·005	1·430	0·120	7·308
470	0·440	0·059	2·350	1·190	0·148	6·298	1·716	0·207	9·050
480	0·500	0·118	2·788	1·319	0·250	7·233	1·884	0·340	10·268
490	0·529	0·189	3·083	1·375	0·407	7·808	1·954	0·537	10·992
500	0·537	0·329	3·272	1·390	0·647	8·138	1·973	0·823	11·390
510	0·540	0·569	3·396	1·394	1·181	8·327	1·979	1·233	11·606
520	0·561	0·960	3·469	1·422	1·529	8·426	2·008	1·798	11·713
530	0·641	1·516	3·510	1·519	2·214	8·477	2·110	2·518	11·767
540	0·815	2·214	3·533	1·725	3·037	8·504	2·324	3·375	11·795
550	1·115	3·024	3·545	2·067	3·963	8·518	2·676	4·328	11·809
560	1·575	3·916	3·550	2·567	4·936	8·524	3·184	5·316	11·815
570	2·228	4·853	3·553	3·234	5·895	8·526	3·846	6·269	11·818
580	3·093	5·790	3·555	4·052	6·785	8·528	4·635	7·128	11·820
590	4·162	6·681	3·556	4·984	7·563	8·529	5·509	7·859	11·821
600	5·382	7·487	3·557	5·973	8·217	8·530	6·410	8·345	11·822
610	6·659	8·183	3·558	6·956	8·749	8·531	7·278	8·929	11·822
620	7·869	8·755	3·558	7·381	9·167	8·531	8·052	9·295	11·822
630	8·891	9·193	3·558	8·650	9·475	8·531	8·672	9·562	11·822
640	9·667	9·505	3·558	9·077	9·687	8·531	9·120	9·742	11·822
650	10·209	9·714	3·558	9·434	9·825	8·531	9·421	9·857	11·822
660	10·554	9·843	3·558	9·656	9·907	8·531	9·608	9·926	11·822
670	10·754	9·916	3·558	9·780	9·953	8·531	9·705	9·963	11·822
680	10·864	9·957	3·558	9·845	9·977	8·531	9·758	9·982	11·822
690	10·923	9·978	3·558	9·878	9·988	8·531	9·784	9·992	11·822
700	10·953	9·989	3·558	9·894	9·995	8·531	9·796	9·996	11·822
710	10·969	9·995	3·558	9·902	9·997	8·531	9·802	9·998	11·822
720	10·977	9·997	3·558	9·905	9·999	8·531	9·805	9·999	11·822
730	10·981	9·998	3·558	9·908	9·999	8·531	9·806	10·000	11·822
740	10·983	9·999	3·558	9·909	10·000	8·531	9·807	10·000	11·822
750	10·984	10·000	3·558	9·909	10·000	8·531	9·807	10·000	11·822
760	10·984	10·000	3·558	9·909	10·000	8·531	9·807	10·000	11·822
770	10·985	10·000	3·558	9·909	10·000	8·531	9·807	10·000	11·822
780	10·985	10·000	3·558	9·909	10·000	8·531	9·807	10·000	11·822

Table 4 (*cont.*). Abscissae for standard illuminants

Wave-length (mμ.)	2360° K.			1900° K.		
	X	*Y*	*Z*	*X*	*Y*	*Z*
380	0·000	0·000	0·000	0·000	0·000	0·000
390	0·000	0·000	0·001	0·000	0·000	0·000
400	0·001	0·000	0·005	0·000	0·000	0·002
410	0·005	0·000	0·022	0·002	0·000	0·008
420	0·018	0·000	0·085	0·007	0·000	0·032
430	0·053	0·002	0·259	0·022	0·001	0·105
440	0·107	0·006	0·528	0·046	0·002	0·226
450	0·170	0·013	0·860	0·076	0·006	0·386
460	0·236	0·026	1·236	0·110	0·013	0·582
470	0·288	0·050	1·580	0·139	0·026	0·773
480	0·318	0·094	1·837	0·157	0·052	0·926
490	0·330	0·171	2·008	0·165	0·101	1·034
500	0·332	0·309	2·124	0·166	0·193	1·112
510	0·336	0·556	2·202	0·169	0·369	1·167
520	0·372	0·953	2·246	0·196	0·668	1·200
530	0·477	1·500	2·272	0·279	1·102	1·221
540	0·685	2·182	2·287	0·452	1·671	1·234
550	1·032	2·979	2·294	0·757	2·370	1·240
560	1·562	3·865	2·297	1·245	3·186	1·243
570	2·314	4·806	2·299	1·960	4·092	1·245
580	3·310	5·752	2·301	2·974	5·045	1·247
590	4·535	6·655	2·302	4·262	5·995	1·248
600	5·919	7·477	2·303	5·778	6·896	1·249
610	7·339	8·189	2·304	7·399	7·709	1·250
620	8·648	8·773	2·304	8·953	8·402	1·250
630	9·710	9·211	2·304	10·262	8·942	1·250
640	10·506	9·522	2·304	11·280	9·340	1·250
650	11·045	9·726	2·304	11·995	9·610	1·250
660	11·380	9·850	2·304	12·454	9·779	1·250
670	11·569	9·919	2·304	12·721	9·877	1·250
680	11·676	9·958	2·304	12·878	9·934	1·250
690	11·732	9·978	2·304	12·962	9·964	1·250
700	11·761	9·988	2·304	13·007	9·981	1·250
710	11·776	9·994	2·304	13·032	9·990	1·250
720	11·784	9·997	2·304	13·046	9·995	1·250
730	11·789	9·998	2·304	13·053	9·997	1·250
740	11·791	9·999	2·304	13·057	9·999	1·250
750	11·792	10·000	2·304	13·058	9·999	1·250
760	11·792	10·000	2·304	13·059	10·000	1·250
770	11·792	10·000	2·304	13·060	10·000	1·250
780	11·792	10·000	2·304	13·060	10·000	1·250

535·337:546·17

NOTE ON ADDITIONAL EXPERIMENTS ON THE EFFECTIVE ROTATION TEMPERATURE OF THE NEGATIVE GLOW IN NITROGEN

By N. THOMPSON, Ph.D.

Received November 14, 1934. *Read in title March* 1, 1935.

ABSTRACT. A summary is given of the results of further determinations of the effective rotation temperature produced when a discharge tube is maintained at a high temperature by external heating, and the form of the relation between the two temperatures is discussed in the light of the revised results.

In a previous publication under the above title[1] certain anomalous results were reported when the nitrogen discharge was produced in a tube surrounded by a furnace at a high temperature (700° C.). In these circumstances it was found that the effective rotation temperature could be less than the furnace temperature. In the discussion which followed the paper it was suggested that this might be a spurious result due to the use of a thermocouple (copper-constantan) unsuited to the temperatures measured. To decide this point, some of the experiments have since been repeated with new couples; the results indicate that the criticism was well founded and the anomaly not real. It seems worth while presenting the amended results in detail however, particularly in view of the recent appearance of another paper on the same subject[2] in which very different conclusions are reached.

The apparatus was identical with the second type described in the previous paper. The gas pressure and the voltage across the tube were of the same order as formerly, being respectively 1·2 mm. ± 0·4 per cent, and 384 V. ± 0·3 per cent, while the current was higher at 30 mA. The temperatures inside the tube were measured with either a tungsten-constantan or a nickel-nichrome thermocouple. The former was calibrated both before and after use (the two calibrations agreeing very well) and the latter after use only. The two instruments gave quite consistent results. It should perhaps be mentioned that the thermocouple reading was taken in every case while the discharge was running. This reading was higher than that which obtained in the absence of discharge, by an amount which decreased with increasing temperature and was about 30° C. at room temperature. The effective rotation temperatures were evaluated as before.

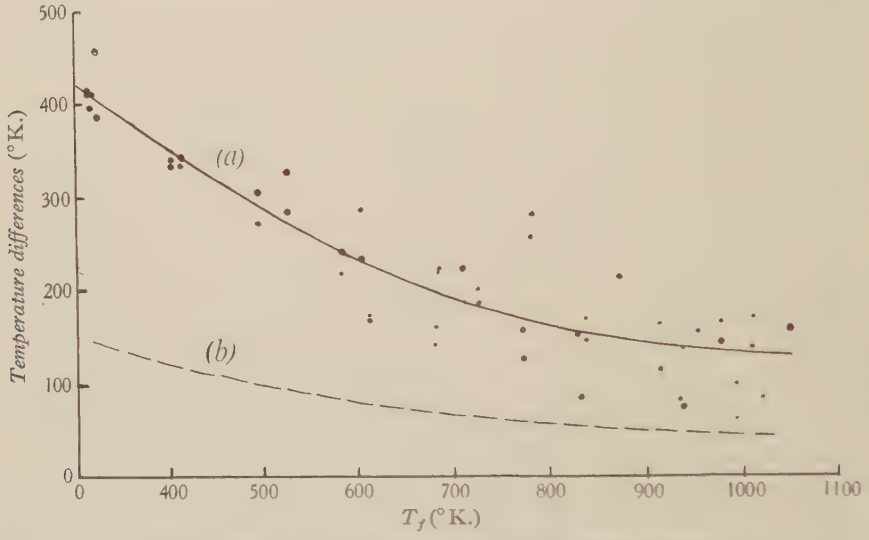
Several independent series of results were obtained, and they are summarized in the appended figure which shows $(\tau - T_f)$ plotted against T_f, where τ is the effective rotation temperature and T_f is the furnace temperature. In agreement with the previous results, this quantity falls with increasing temperature, but the earlier conclusion that it eventually becomes negative is not confirmed. The shape of the smoothed curve is essentially the same as that showing the temperature T_c

τ

T_f

T_c

of the cathode in figure 5 of the earlier paper. The cathode temperature was not measured in these later experiments, but the earlier results may be taken as indicating roughly the general run of the curves, since both T_c and T_f depended ultimately on the same faulty thermocouple calibration. On this basis the probable shape of the curve showing $(T_c - T_f)$ against T_f is indicated in the figure by the dotted line, which is taken from figure 5 of the original paper. Although the two sets of results are not quantitatively comparable, there is no doubt whatever that the effective rotation temperature is higher than the temperature of the cathode at low temperatures (compare figures 3 and 5 of original paper) and it is also very probable that it always remains the higher of the two, as shown in the accompanying figure.



Curves showing (*a*) $(\tau - T_f)$ and (*b*) $(T_c - T_f)$ plotted against T_f.

If we continue, in default of any better estimate, to take T_c as an indication of the true gas temperature, these results show that the effective rotation temperature is higher than the gas temperature, as was found by Duffendack. On the other hand, that author's conclusion that the former temperature is independent of the latter is certainly not borne out. In the same paper he suggests that the difference $(\tau - T_c)$ may be due to an increase in the mean rotational kinetic energy of the molecule brought about directly during the exciting collision process. This hypothesis, however, does not seem able to account for the marked variation of this quantity with temperature, which is shown by the above graph.

It is a pleasure to express my thanks to Prof. Milner of Sheffield University for providing the facilities which enabled me to carry out these later experiments.

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535·338.4:546.45–31

THE BAND SPECTRUM OF BERYLLIUM MONOXIDE

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ABSTRACT. It is shown that certain band-heads previously unaccounted for in the ultra-violet spectrum of BeO can be fitted by means of the equation

$$\nu_h = 29753{\cdot}0 + 1083{\cdot}1\,(v' + \tfrac{1}{2}) - 11{\cdot}1\,(v' + \tfrac{1}{2})^2 - 1148{\cdot}7\,(v'' + \tfrac{1}{2}) + 11{\cdot}6\,(v'' + \tfrac{1}{2})^2.$$

It is suggested that the final level of these bands is the same as the initial level of the near infra-red bands (i.e. a $^1\Pi$ level) and it is also suggested that both the ultra-violet BeO systems are of $^1\Pi \rightarrow {}^1\Pi$ type.

§ 1. INTRODUCTION

Excitation of the BeO molecule gives rise to a number of band systems. Two of these have been analysed in detail and have been shown to be $^1\Sigma \rightarrow {}^1\Sigma$ and $^1\Pi \rightarrow {}^1\Sigma$ respectively, lying in the blue-green in the first instance[1,2] and in the near infra-red in the second[3]. Band emission has also been observed in the near ultra-violet. Jevons[4] was the first to observe this but made no analysis; Bengtsson (*loc. cit.*), however, succeeded in making a vibrational analysis which accounted for some of the bands, although quite a number were not included. The purpose of this note is to indicate how these remaining bands may be accounted for.

§ 2. EXPERIMENTAL DETAILS

For the analysis of the $^1\Sigma \rightarrow {}^1\Sigma$ bands[1,2] the spectrum had been excited by the burning of a beryllium salt in the carbon arc. In the present work a number of spectrograms were obtained in this way but the long exposures, coupled with the fact that such an arc requires constant attention, led us to make use of the metallic beryllium now obtainable and to run an uncondensed spark between two electrodes of the metal. Such a spark will run unattended for many hours. (The arc between electrodes of metallic beryllium was used by L. Herzberg[3] and was found to require constant attention.) The spectrograms were obtained in the first and second orders of the 21-ft. grating now mounted in this department. Comparison spectra from an iron arc were put on the plates by means of a set of shutters controlled from outside the grating room itself.

§ 3. THE ULTRA-VIOLET BAND SYSTEMS

Bengtsson succeeded in describing a number of the bands by means of the equation:

$$\nu_h = 31899 + 1006n' - 10n'^2 - 1126n'' + 10n''^2 \quad \ldots\ldots(1).$$

Rewriting this in terms of the new quantum theory and the accepted notation ([5], p. 26), we get

$$\nu_h = 31959 + 1016\,(v' + \tfrac{1}{2}) - 10\,(v' + \tfrac{1}{2})^2 - 1136\,(v'' + \tfrac{1}{2}) + 10\,(v'' + \tfrac{1}{2})^2 \quad \ldots\ldots(2).$$

At the time when this analysis was made only the blue-green $^1\Sigma \rightarrow {}^1\Sigma$ bands had been analysed and it was clear that this new ultra-violet system was unrelated to the $^1\Sigma \rightarrow {}^1\Sigma$ system. The analysis of the near infra-red system by L. Herzberg, however, showed that these were of $^1\Pi \rightarrow {}^1\Sigma$ type, where the lower level was also the lower level of the visible $^1\Sigma \rightarrow {}^1\Sigma$ bands, and that their vibrational structure could be represented by the equation

$$\nu_o = 10542{\cdot}91 + 1127{\cdot}771\,(v' + \tfrac{1}{2}) - 8{\cdot}4007\,(v' + \tfrac{1}{2})^2 + 0{\cdot}03913\,(v' + \tfrac{1}{2})^3 - 1486{\cdot}87\,(v'' + \tfrac{1}{2}) + 11{\cdot}70\,(v'' + \tfrac{1}{2})^2 \quad \ldots\ldots(3).$$

Herzberg concluded that the ultra-violet and infra-red systems had the $^1\Pi$ level ($\omega_e = 1128$ cm.$^{-1}$) in common and that the higher value of the vibrational frequency given by the ultra-violet bands ($\omega_e = 1136$ cm.$^{-1}$) was due to the fact that equation (2) applied to heads, whilst equation (3) applied to origins. The deviation shown by the value obtained from the heads is to be expected, since the moment of inertia of the molecule in the two states is not very different (as is shown by the values of the vibrational frequencies of the two states) and the bands degrade to the red.

Equation (2) does not account for a number of heads commencing at λ 3364 and running to the red. These bands formed the strongest feature of the ultra-violet spectrum as we observed it, but no analysis was possible until the side sequences had been obtained. These are extremely faint, even on our heaviest plates, the $(+1)$ sequence overlaps the (-1) sequence of Bengtsson's system, and the heads are very poorly defined. It was found possible, however, to fit these heads by the formula

$$\nu_h = 29753{\cdot}0 + 1083{\cdot}1\,(v' + \tfrac{1}{2}) - 11{\cdot}1\,(v' + \tfrac{1}{2})^2 - 1148{\cdot}7\,(v'' + \tfrac{1}{2}) + 11{\cdot}6\,(v'' + \tfrac{1}{2})^2 \quad \ldots\ldots(4).$$

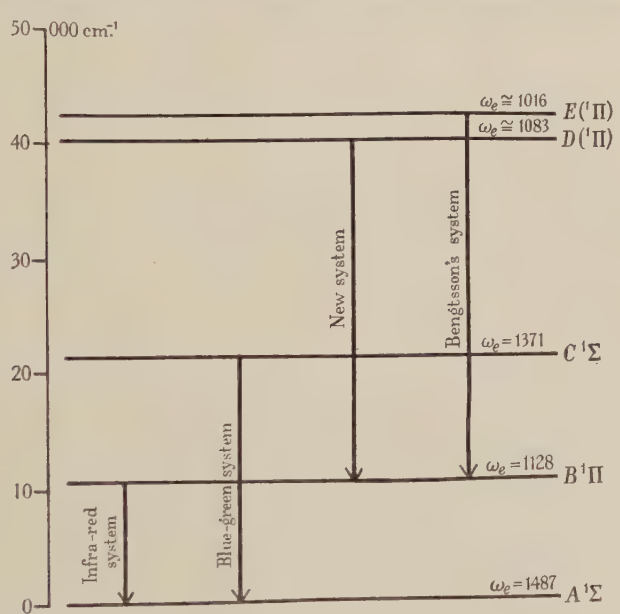
The fit given by this equation is shown in the table.

Table. Vibrational analysis of the D $^1\Sigma$ – B $^1\Pi$ system. (Wave numbers in brackets calculated from equation (4))

v' \ v''	0	1	2	3
0	29720·8 (29720·3)	28595·7 (28594·9)	—	—
1	30783·6 (30781·1)	29655·3 (29655·7)	28551·6 (28553·3)	—
2	—	30689·6 (30694·5)	29593·7 (29592·1)	28512·8 (28513·1)
3	—	—	30610·0 (30608·5)	29530·2 (29529·5)

It seems likely that the lower level here is the $^1\Pi$ level already discussed. The vibrational frequency (1148·7 cm.$^{-1}$) is higher again than the one obtained from the other ultra-violet system, but in the present case the moments of inertia in the two states are much more nearly equal (as is shown by the closer approach to equality of ω' and ω'') and therefore the heads will be formed at very considerable distances from their origins, and this distance $(\nu_h - \nu_o)$ will differ markedly from sequence to sequence.

The electronic levels and transitions now known in the BeO spectrum are shown in the figure. In view of the unknown character of the two highest states, and in order to simplify future reference to the various systems, we have used the notation employed by Jevons ([5], pp. 76, 284) to describe the BeO levels but have used the labels D and E tentatively put forward by him in a rather different way.



§ 4. ROTATIONAL STRUCTURE

The nature of the two states D and E cannot be decided until a rotational analysis has been carried out in each case for bands involving these levels. We were hopeful that it would prove possible to do this for the new D $\rightarrow$ B $^1\Pi$ system since a considerable amount of structure was visible on our plates. Unfortunately, owing to the weakness of the side sequences, it was only found possible to study the main ($\Delta v = 0$) sequence. But even here unmistakable branches were only discernible in the (0, 0) band. This was due to the fact that, at the high temperature of either the arc or the spark, the maximum intensity of the various branches occurs at high values of J, so that the higher members of the $\Delta v = 0$ sequence were overlaid by branches from other bands to such an extent that analysis was impossible.

However, even with only the (0, 0) member of this sequence available, a definite conclusion as to the constants of the upper level involved in this system would have been possible had combination differences for the lower ($B^1\Pi$) level been obtainable from the analysis made by L. Herzberg of the $B^1\Pi \rightarrow A^1\Sigma$ system. Unfortunately, however, the analysis of this $B^1\Pi \rightarrow A^1\Sigma$ system gave only the B-values of the $B^1\Pi$ level from $v=2$ to $v=7$, although by extrapolation of the equation for these B-values B_0 should be 1·342. Similarly by extrapolation $D_0 = -7{\cdot}7 \times 10^{-8}$. Knowing these values we can calculate the term differences for the $B^1\Pi$ ($v=0$) state.

These same differences should, of course, have been obtainable from the (0, 0) band of the $D \rightarrow B^1\Pi$ system. We observed two branches in this (0, 0) band but could get no definite agreement between the differences obtained from these branches and the calculated differences. We did, however, succeed in getting an arrangement of the branches which, on treatment of the differences in the usual manner, gave practically a constant value for B_0', whilst the B_0''-values were too high (in comparison with the 1·342 obtained above) by some 2 per cent for low J-values although they approached the extrapolated value at higher J-values, and settled down within 0·5 per cent of the expected value. The constancy of the B_0'-values is inexplicable if our arrangement of the lines in the branches is faulty, whilst the behaviour of the B_0''-values is equally difficult to explain if our analysis is correct. It could, of course, be accounted for by assuming a perturbation of the $B^1\Pi$ ($v=0$) level, but this would not be a justifiable assumption in view of the paucity of our data.

We are, however, convinced that the two branches observed in the (0, 0) band are genuine, and that the second differences of the lines in the branches enable us to estimate the difference $B_0' - B_0''$ as $-0{\cdot}06$. If our vibrational analysis is correct, then $B_0' = 1{\cdot}28$, i.e. this is the B-value for the level D ($v=0$).

As regards the nature of the two levels D and E it seems probable that both are of $^1\Pi$ type, since in both the $D \rightarrow B^1\Pi$ and $E \rightarrow B^1\Pi$ systems only single heads have so far been observed. If the transitions were of such a type that $\Delta\Lambda = 0$, then double heads would, presumably, be a marked feature of the spectrum. Actually the only head of any intensity unaccounted for, in the region of the spectrum that we are considering, is one at 29,683 cm.$^{-1}$ It is not certain that this is a head. It may be an atomic line, but we have been unable to account for it as such. Its appearance is that of a moderately strong line diffuse to the red. It is possible that this is a Q head associated with our (0, 0) head, which is presumably of R type, at 29,720 cm.$^{-1}$ According to our conclusion that the transition is probably of $^1\Pi \rightarrow {}^1\Pi$ type, and that the B_0-values are as suggested earlier, a weak Q head might be observable in this vicinity.

Finally, it is of interest to note that some very heavily exposed plates of the $C^1\Sigma \rightarrow A^1\Sigma$ system have been obtained and that no evidence for the existence of an isotope Be^8 is obtainable from them.

§ 5. ACKNOWLEDGMENTS

We take this opportunity of thanking Prof. Bragg for the facilities that have been placed at our disposal and Prof. Curtis for kindly reading the manuscript.

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THE EFFICIENCY OF EXCITATION OF THE NITROGEN FIRST POSITIVE BANDS BY ELECTRON IMPACT

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ABSTRACT. A determination has been made of an upper limit to the effective target area of the nitrogen molecule for excitation to the triplet levels by electron impact. Observations were made on the visible groups of the first positive system by the use of an electron tube previously described. By calibrating the plate with a lamp, the absolute emission of which was found in comparison with a black-body radiator, the rate of emission of quanta in each group was calculated, and with the aid of the radiometric analyses available was extended to the whole of the first positive system. The cross-sectional area, for excitation by electrons with energy of about 14 volts, is, in terms of the area of the first Bohr orbit, found to be 5×10^{-2}, with an estimated probable error of 35 per cent.

In many problems connected with the electric discharge in nitrogen, the existence of metastable molecules in the $A^3\Sigma$ state plays an important role. It is therefore of interest to form some estimate of the rate of supply of these excited molecules by electron-collision under controlled conditions, i.e. to estimate the effective target area which a nitrogen molecule presents to an electron for the purpose of being excited to the metastable level.

The $A^3\Sigma$ level may be excited either directly or by cascade from the other triplet levels. The probability of direct excitation cannot be estimated spectroscopically because of the low intensity of the $A^3\Sigma - X^1\Sigma$ intercombination system and also of the small chance of a metastable molecule making this transition before its energy is otherwise dissipated. On the other hand, cascade excitation is accompanied by emission of the first positive band system, and an estimate of the number of quanta emitted in this system gives at once the number of molecules in the $A^3\Sigma$ state produced in this way under the given experimental conditions.

This note gives an account of an absolute determination of the effective target area of the nitrogen molecule for production of the first positive system by collision with electrons of such energy that the emission of radiation in this band system is approximately a maximum; i.e. an upper limit is given to the effective cross-section for production of molecules in the $A^3\Sigma$ state by cascade. At the same time this result is also a rough estimate of the maximum efficiency of production of metastable molecules by both processes, because, although direct excitation might

onceivably be much more important when electrons of smaller energy are present, nce the $A^3\Sigma$ excitation function has in all probability a maximum within a few olts of its excitation potential, the possibility of excitation by cascade is under these onditions correspondingly reduced. The relative orders of magnitude of the cross-ectional areas for excitation of molecular and atomic levels are also of interest.

The apparatus previously used to investigate the excitation function of the econd positive bands has been described elsewhere[1]. It consists of an indirectly eated cathode, slit system, and field-free observation chamber, through which itrogen was allowed to pass in a continuous stream at a pressure of about 0·002 mm. he maximum electron energy was about 15·75 volts, and 90 per cent of the ectron current was comprised in a range of about 4 volts below this value. An nage of the electron beam was focused on the slit of a Hilger constant deviation pectrograph.

The radiation-intensity was small and, with the Ilford hypersensitive panchro-natic plates used, exposures of about an hour were necessary. These plates are, of ourse, sensitive only to the visible of the several groups of bands in the first ositive system. But Pfund[2] and Poetker[3] have published radiometric analyses f the complete system, and it was therefore found more convenient to deduce rom them the proportion of the total energy of the system contained in each group han to use special infra-red plates and photograph the whole system. The plates ere calibrated by means of continuous spectra of equal exposure-times and varying lit-widths, obtained from a lamp run at a known colour temperature and placed t a convenient distance from the spectrograph with no intervening optical system.

As the slit of the spectrograph was sufficiently wide to ensure complete mergence f the rotational structure, the images could be treated as a continuous spectrum. Owing to the effect of spreading discussed in another paper[1], the emission of ght was not confined to the dimensions of the electron beam, so that the image eceived on the plate was a blurred patch with no sharply defined boundaries. his was photometered in a direction normal to the dispersion at intervals of mm. measured parallel to the dispersion, the centre of one vibration band, just esolved, being taken as datum point. With the aid of the plate-calibration curves or each of these cross-sections (necessary owing to the rapid change in plate-ensitivity in this region) intensity contours could be built up, and the total intensity f the group could be found by integration. This was then expressed in equivalent ntensity units per square millimetre; i.e., as if the whole of the intensity in the roup were integrated and averaged over one square millimetre centred on the iven wave-length, the value found being regarded as equivalent to that of the ontinuous spectrum with a slit of appropriate width.

For lack of absolute calibration of the tungsten lamp, a comparison was made, y means of a Hilger-Nutting photometer, with the cavity radiation from an alumina ylinder at a temperature of about 1000° C. Assuming that the lamp radiates in he manner of a black body, the absolute temperature of which is equal to the olour temperature of the lamp, it is possible to calculate for the latter an effective rea of the emitting surface which, of course, varies with the wave-length owing to

the changing spectral emission of tungsten. The appropriate value of this quantity is then used in Planck's radiation formula to calculate the rate of emission of quanta of a given wave-length, the spectral range $d\lambda$ in the formula being determined by the dispersion of the spectrograph at this point, since the length of spectrum considered on the plate is 1 mm.* The number of quanta falling on a square millimetre of plate then depends on the distance of the lamp from the slit and on the dimensions of the latter, i.e. its width per division and its length effective in producing a spectrum 1 mm. in depth, as given by the reciprocal of the magnification of the camera. Let this number be n. Then if the equivalent intensity of the band, in divisions of slit-width, is m, and the ratio of exposure times of band and continuous spectrum is R, the rate N at which quanta are photographed in the band is equal to nm/R^p, where p is the Schwarzchild factor for the plate, and is the weighted mean of all observations of intensity in the band, owing to its variation with plate-blackening. From the geometry of the optical system used in photographing the beam the total number of quanta emitted in the band can be determined, and an analysis of the radiometer curves enables a calculation of a similar quantity for the whole system.

The measured gas pressure and estimated temperature give the number of molecules per cubic centimetre, and the electron current is known. From a knowledge of the slit-width and relative positions of the slit, focusing lens and beam, the length of the latter under observation can be found. The calculation of the effective cross-section is then quite simple.

The table shows the principal data used in four calculations of the effective cross-section. They are taken from each of the two visible groups of first positive bands, obtained in photographs with exposures of 1 and 2 hours respectively. The effective area is given in terms of πa_0^2, the area of the first Bohr orbit, a_0, having the value 0·528 A.

Group	Equivalent intensity (slit-div./mm²)	Percentage of total quanta in system	Exposure (min.)	Pressure (mm. Hg. × 10⁻³)	Current (m.A.)	$\pi r^2/\pi a_0^2$
6500 A.	29·3	19	120	1·55	0·98	$5{\cdot}26 \times 10^{-2}$
	16·5	19	60	1·7	1·0	$5{\cdot}14 \times 10^{-2}$
5900 A.	16·7	4·5	120	1·55	0·98	$5{\cdot}17 \times 10^{-2}$
	8·3	4·5	60	1·7	1·0	$4{\cdot}85 \times 10^{-2}$

Mean of $\pi r^2/\pi a_0^2$, $5{\cdot}1 \times 10^{-2}$.

The accuracy of this result is difficult to assess, owing to the large number of independent factors which enter into the problem. Whilst the consistency of the four determinations is very satisfactory, the extreme deviation being only 5 per cent

* Since comparisons with the black body were made at the wave-lengths required in the calculation a knowledge of the colour temperature of the lamp is rendered unnecessary, as the exponential factor involving this quantity cancels out.

is thought that the probable error should be placed at the higher figure of 35 per ent. Of this, 8 per cent is accounted for in the determination of the absolute mission from the lamp, 10 per cent in the equivalent intensities, and 10 per cent the relative numbers of quanta in each group of the system.

I am indebted to Dr C. H. Johnson, of the Chemical Department, for assistance the use of a Hilger-Nutting spectrophotometer, and to the Director of the ford Research Laboratories for a determination of the Schwarzchild factor of the hotographic plates. In particular, I desire to express thanks to Dr E. T. S. ppleyard for much helpful advice, discussion of the problem, and assistance in hecking the calculations.

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621.327.31 535.337:546.49

ABSOLUTE INTENSITIES IN THE SPECTRUM OF QUARTZ MERCURY ARCS AND THEIR VARIATION WITH TEMPERATURE-CHANGES OF THE SURROUNDING AIR

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ABSTRACT. Variations in intensity of the more important lines in the mercury arc spectrum are investigated as the temperature of the air surrounding the burner is increased. The intensity and arc watts reach maxima but not quite together. Empirical relations are found connecting intensity and electrical input. Absolute intensities of some thirty lines between 7000 and 2300 Å. emitted by commercial quartz mercury-vapour burners are tabulated and some theoretical aspects of the results are discussed.

§ 1. INTRODUCTION

Mercury-vapour burners are usually operated in some form of housing, and as the intensity of radiation emitted is susceptible to changes of temperature it is of interest to know how it varies as the temperature of the surrounding air increases. In different housings a given burner will attain equilibrium at different electrical ratings depending on the ventilation.

In the investigation to be described, the temperature of the air around several quartz mercury-vapour burners was varied and the intensity of some of the most prominent lines in the spectrum was determined, the supply voltage and ballast resistance being maintained constant. Results have been quoted bearing upon the variation in intensity when the supply volts are varied[1], and Harrison and Forbes[2] have described a special type of lamp wherein all the variables were separable and the effect of varying either the voltage across or the current through the tube was determined. Variations of intensity with change of voltage-gradient, for constant current, have been given by Taylor[3]. Our object was to investigate the changes that might occur in the practical operation of commercial mercury-vapour burners, i.e. the intensity-variations resulting solely from temperature-changes such as are due to operation of the burners in housings differing in ventilation.

A complete investigation was also made of the absolute intensities of some 30 lines between 7000 Å. and 2300 Å. in the spectrum from quartz mercury arcs, wherein the intensity due to the whole of the burner at a distance of 1 metre was determined. From such results therapeutic, bactericidal and other effects can be deduced if desired. Some theoretical aspects of the results are discussed.

§ 2. PROCEDURE

The burner was placed 117 cm. from the entrance slit of a spectrometer so that adiation from the whole arc-length entered the instrument; a thermopile, after he exit slit, connected to a Paschen galvanometer (the combination having been alibrated by means of a carbon filament lamp standardized by the National hysical Laboratory) gave the intensity after transmission through the spectro-eter*; losses in this latter were determined experimentally by means of an uxiliary monochromator and thus the actual intensity at the entrance slit could e determined for any wave-length.

The temperature of the air surrounding the burner was decreased by means of fan or increased by means of an electric heater immediately below the burner. was not practicable nor was it considered necessary to determine the actual emperature of the burner at any point; as will be seen later, the conditions of peration can be inferred from the electrical characteristics.

The exit slit was set wider than the collimator slit in order that the intensity f lines close together might be integrated by the thermopile and the intensity or the group obtained, rather than that for each individual line comprising the roup. The wave-lengths studied were 5790, 5770 A. together; 5461 A.; the 358-A. group; the 3650-A. group; the 3126-A. group; 3022 A.; the 2652-A. roup; and 2535, 2537 A. together. Their intensities were determined for various quilibrium conditions of the burner brought about by cooling or heating as escribed, and the electrical conditions also were noted.

§ 3. RESULTS AND DISCUSSION

Variation of intensity. As is generally known, the intensity of all the spectral nes increases as the ambient air-temperature increases, and at the same time the rc watts increase, eventually passing through a maximum and then decreasing; he intensity, however, continues to increase after this maximum of power has een reached until, on further heating of the surrounding air, this also soon reaches maximum and then begins to decrease. Typical curves showing the variation of ntensity with arc watts due to changes in air-temperature for a 2·5-A. burner† perated on 240-V. mains with a series resistance of 36 Ω.) are given in figure 1, nd the maxima for watts and intensity are clearly shown. The primary variable is, f course, the temperature of the air in the immediate vicinity of the burner, and elated variables are the temperature of and pressure within the burner itself.

The arc voltage and current are good indications of the conditions under which

* A null method was used as being more practicable in overcoming disturbances and drift. A eries and shunt resistance circuit injected an opposing current into the galvanometer circuit, witching taking place automatically as the light-shutter was raised; the balancing potential across he main potentiometer, as read on a sub-standard voltmeter, gave the required experimental bservations proportional to the intensity.

† Normal operating conditions for this burner, with the specified mains voltage and ballast esistance, is 2·5 A. which is the current-value for ventilation given in a normal housing with free air irculation.

the burner is operating, for as the temperature of the air is raised from the coolest to the hottest degree practicable, the arc volts increase whilst the current decreases. Since the supply volts, E_s, and ballast resistance, R, are maintained constant (E_s, R) the arc volts E and current i (E, i) are related linearly, the characteristic having a negative slope numerically equal to the series resistance R. For

$$E = E_s - Ri \qquad \text{.....(1).}$$

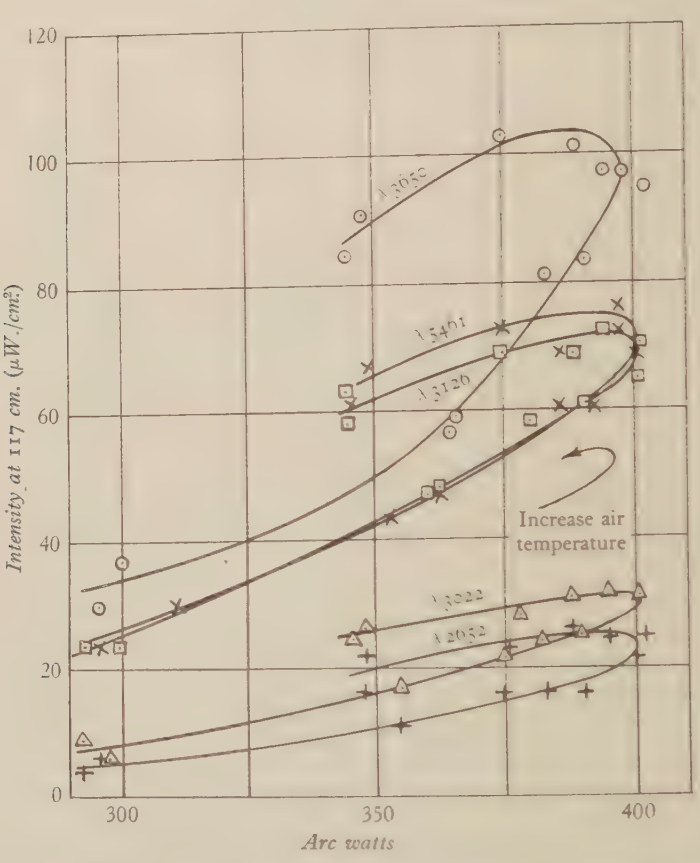

Figure 1. Arc watts and intensity due to temperature-variation of air around burner no. 844. Mains voltage, 240 V.; ballast resistance, 36 Ω.

Now the arc watts $P = Ei = E_s i - Ri^2$; differentiation shows that P (P) is a maximum when $i = E_s/2R$ giving

$$P_{max.} = E_s^2/4R \qquad \text{.....(2).}$$

$P_{max.}$ as found by experiment was 400 W. and is also 400 by substitution in equation (2) of $E_s = 240$ V. and $R = 36\ \Omega$.

The maximum intensity occurs at a temperature such that the arc watts are a little less than their maximum; thus maxima for λλ 5780, 5461, 4358 occur at about 385 W. whilst maxima for λλ 3126, 3022, 2652, 2536 occur at about 396 W. and a maximum for λ 3650 occurs at about 380 W. In the ultra-violet region of

wave-lengths from λ 3126 downwards, the maxima of intensity all occur very near the maximum wattage, the peak being sharper than for long wave-lengths. For maximum intensity, therefore, this burner should be operated with such ventilation that the arc watts lie between 385 and 400 at the higher voltage, i.e. between 120 and 140 V. with corresponding currents of 3·3 and 2·75 A.; the normal operation is at 2·5 A., which occurs at 150 V. (375 W.), and though the intensities are not quite at their maxima they are nearly so and operation at any voltage between 120 and 150 will be satisfactory and ensure that only small changes of intensity shall occur with any temperature-fluctuations. Under these conditions the intensity is only subject to small variations for quite large temperature-changes, and this range is the most suitable for operation. That all lines exhibit decreased intensities when such a burner is operated under extra hot conditions is shown by comparison of columns 2 and 3 in table 2.

Exactly similar results were obtained with a 3·5-A. burner and 28-Ω. series resistance, the maxima of arc wattage again not producing maxima of intensity. Maximum power was 515 W. by experiment and 514 by substitution in equation (2). The maximum intensity for $\lambda\lambda$ 5461, 4358 and 3126 occurred at about 505 W., that for $\lambda\lambda$ 3650, 3022, and 2536 at 510 W.; thus, in this case also, for maximum intensity the burner should be operated at such a temperature that the voltage lies between 120 and 140 with corresponding current-values of 4·28 and 3·56 A., normal operation being at 3·5 A., 141 V. and 494 W. These two types of burner have the same arc-length, about 12 cm., and it is to be noted that maximum intensity occurs for both types within the same voltage-range, i.e. with the same value (10 to 11·7) of volts per centimetre, the greater arc current being responsible for the greater actual intensity.

Between arc voltages of 80 and 140 the foregoing experimental results can be expressed by the relation

$$I = CiE^n \qquad \text{.....(3),}$$

where I is the intensity of radiation of some particular wave-length and C and n are constants corresponding to that wave-length but differing for each spectral line. This is a relation between I, i and E when the supply volts and series resistance are constant and the only variable is the temperature of the air around the burner, i and E being further related by equation (1). Plotting of $\log_{10}(I/i)$ against $\log_{10} E$ results in the type of curve shown in figure 2, where the values for some of the wave-lengths of the 2·5-A. burner are given, these being typical of all the results. The linear relation is quite well defined between 80 and 140 V. but below this the curve departs considerably from linearity. Above 140 V. there is a marked change in slope, but the exact form is difficult to determine since it was not found possible to extend the observations much above the points given. Further rise of temperature increased the pressure in the arc space so much that the arc was extinguished.

I, C, n

Values for n and C as determined from the linear portion of the curves are given in table 1, I being in μW./cm.^{2} at 117 cm. distance and i and E in amperes and volts respectively.

Table 1. Values of n and C for equation (3)

λ	2·5-A. burner		3·5-A. burner	
	n	C	n	C
5780	1·93	0·0017	—	—
5461	1·74	0·0049	1·66	0·008
4358	1·75	0·0040	1·57	0·0115
3650	1·99	0·0021	1·86	0·0046
3126	1·77	0·0045	1·42	0·026
3022	1·92	$0{\cdot}0008_8$	2·11	$0{\cdot}0004_6$
2652	2·24	$0{\cdot}0001_4$	1·76	$0{\cdot}0016_5$
2536	1·88	$0{\cdot}0011_5$	1·48	0·0092

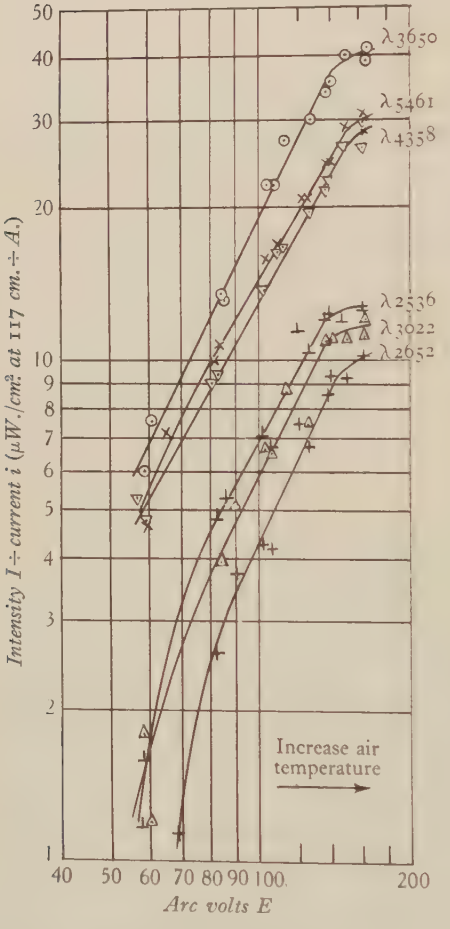

Figure 2.

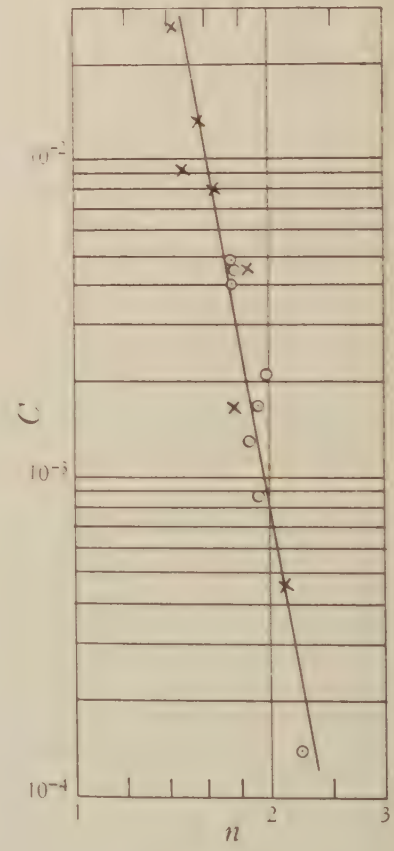

Figure 3.

Figure 2. Relation between intensity current and arc volts as temperature of air around burner is increased. Burner, mains voltage and resistance as in figure 1.

Figure 3. Relation between n and C. × Burner no. 160, 3·5-A. type; ⊙ burner no. 844, 2·5-A. type.

It will be seen that n is different for each wave-length, and this shows that the relative distribution of intensity throughout the spectrum will vary with the operating conditions; thus, for example, as λ 3650 has a large slope or large n the excess of its intensity over that of other wave-lengths will be greater at high temperatures than at low; a similar observation holds for $\lambda\lambda$ 5780, 3022 and 2652. C and n appear to be related, for on plotting $\log_{10} C$ against $\log_{10} n$, figure 3, we find that the points are distributed more or less evenly about a straight line which apparently fits the data from both the 2·5-A. and the 3·5-A. burners owing, no doubt, to the equal arc-lengths. From figure 3 we have

$$C = 1{\cdot}8 n^{-0{\cdot}0082} \qquad \ldots\ldots(4).$$

Differentiation of equation (3) gives $I_{\max.}$ as occurring at about 150 V. which, as we have seen, is beyond the region for which the relation holds, and hence this operation is inapplicable.

A somewhat similar expression is obtained by Asada[4] for the variation of intensity with change of terminal voltage, though full details of his results are not given. He obtains $I = Ki\,(E - E_0)^n$ subject to the condition that the potential difference be not very small, and states that the radiations of longer wave-lengths increase more rapidly than those of shorter. E_0 is the arc voltage on first striking. E_0

Absolute intensities. The results presented in the preceding section were obtained as part of a more complete investigation wherein were obtained the absolute intensities of all the main wave-lengths between 7000 and 2300 A. emitted by several mercury vapour burners and measurable by the radiometric method already described. Most of the intensities were determined for a 5-cm. length of arc at 45 cm. from the collimator slit, and by means of an open thermopile and three filters (passing λ 5461, λ 4358 and all wave-lengths less than 1·4μ) a mean ratio was determined for obtaining the intensity due to the whole arc length at 100 cm. distance. Data thus obtained are summarized in table 2. Columns 3, 4, 5 relate to burners operated under such ventilation conditions as to permit operation with their normal current. Column 2 for no. 793 gives the intensity for this burner operated under much hotter conditions, such as obtain in a closed lamp-house with little air-circulation, and the decrease that results is at once evident. No. 844 was a new burner whilst no. 793 had been in operation before and the loss of intensity for the shorter wave-lengths was becoming apparent.

Since λ 2537 spreads out on the long-wave side to about λ 2587 and the slit was insufficiently wide to accommodate this range, a factor was obtained from microphotometer records of this region whereby the total intensity of all of $\lambda\lambda$ 2537 and 2535 could be obtained from measurements made with the spectrometer set at λ 2536. From such records, also, the amount to be deducted from the reading at λ 2576 due to λ 2537 was deduced, the intensity-values in the table being those of λ 2576 alone.

These intensity-measurements cover a wide range of wave-lengths and it is interesting to note the decay of intensity in the sharp ($2^3P_{0,1,2} - m^3S_1$) and diffuse ($2^3P_{0,1,2} - m^3D_{1,2,3}$) series. In figure 4 are plotted the logarithm of the intensity

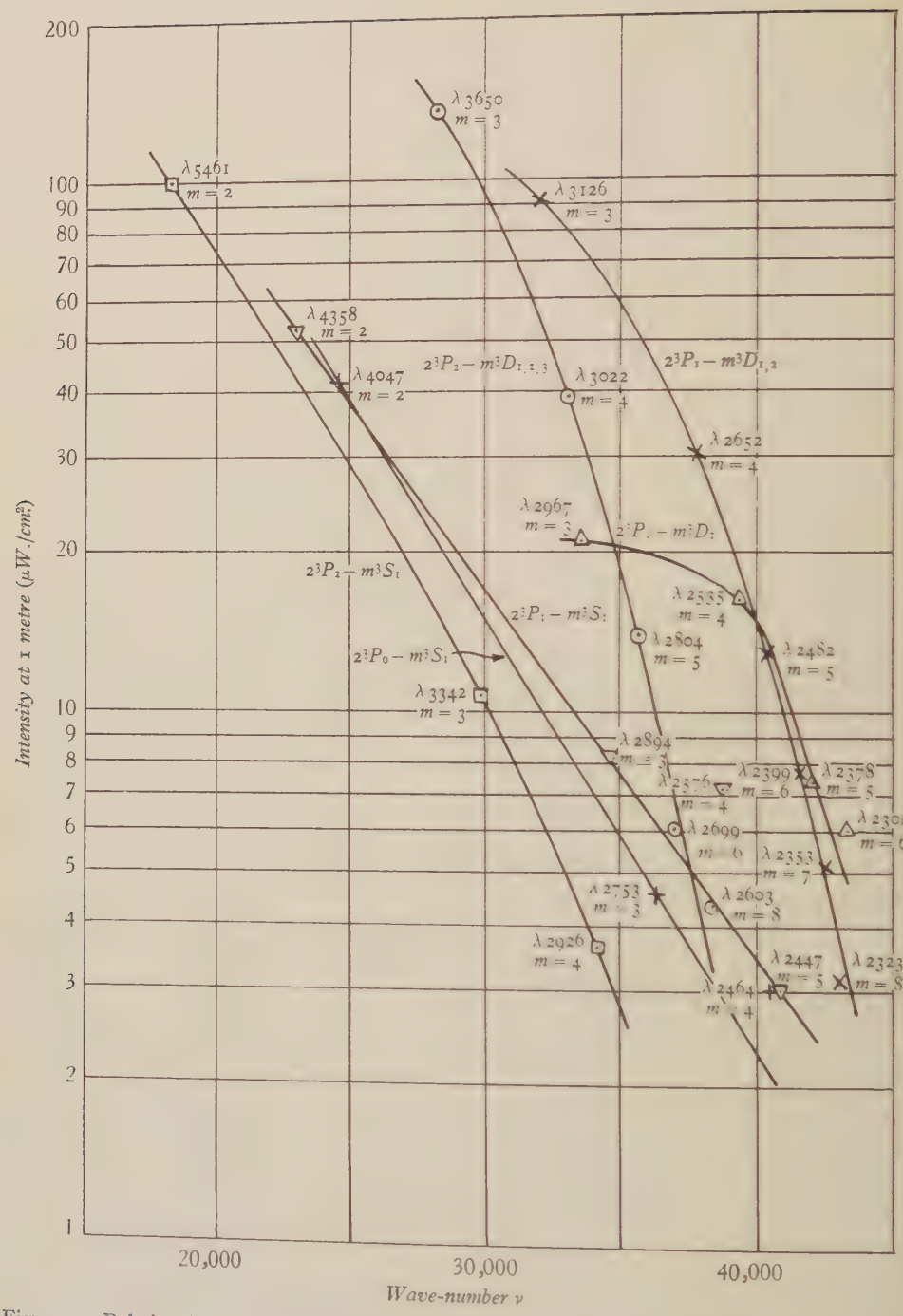

Figure 4. Relation between intensity and wave-number for the sharp and diffuse series of the mercury spectrum. Burner, mains voltage, and ballast resistance as in figure 1; arc voltage 146·4, arc amperage 2·49.

against wave-number for the lines belonging to these series; these are for burner no. 844 and are typical of all the results. Smooth curves can be drawn through practically all the points in a given series and this indicates that experimental errors were small. These results are in agreement with those of McAlister[5], and the curves, like his, appear to approach asymptotic lines of approximately the same slope for the two sets of series; this slope is greater for the diffuse series, a fact which indicates a lower temperature of the excited atoms for the 2^3D than for the 2^3S levels as was pointed out by Hulburt[6]. Hulburt argues that if there is a sort of temperature-equilibrium in the mercury arc, then the intensity I of radiation of wave-number ν is

$$I = \alpha \exp(-hc\nu/kT) \qquad \ldots\ldots(5),$$

where α represents the various probabilities of state and of transition and the usual meanings attach to the other symbols. If α is constant for the lines of a series, the logarithm of the experimental intensity plotted against wave number should be a straight line for the series. Our work and that of McAlister shows that α is not constant but varies with ν, decreasing as ν increases. The change of α with ν is greater in the diffuse series and small in the sharp series, the lines of the latter in some cases being linear, although we have insufficient points to be able to argue this rigorously. From the high-frequency ends of the curves, where they have become practically linear, we deduce approximate temperatures of 6700° K. for the sharp and 2500° K. for the diffuse series, these estimates being based on the four sets of intensity-measurements given in table 2.

In the plot of log I against ν, the intensities of λ 4358 and λ 4339; λ 4078 and λ 4047; λ 2537 and λ 2535 were separated as these pairs are not of the same series. This was done either by means of the microphotometer records or by taking intensity-readings at the separate wave-lengths and calculating the amount to be deducted in respect of the overlap of the neighbouring line. λ 2576 does not fit the general curve in any of the four sets of results, though the linearity of the series to which this belongs is borne out by the fit of λ 2447.

§ 4. ACKNOWLEDGMENTS

Thanks are due to the Thermal Syndicate Ltd. for permission to publish this paper. The investigation was carried out in their Laboratories and the arcs experimented upon were their standard 2·5-A. and 3·5-A., 220–250-V., d.-c.-type quartz mercury vapour burners.

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Table 2. Radiant energy flux (μW./cm^2) at 1 metre from the centre of quartz mercury vapour burners

λ	2·5-A. type. 240-V. mains. 36-Ω. series resistance		3·5-A. type. 240-V. mains. 28-Ω.	
	No. 793		No. 844	No. 160
	Extra hot 162·0 V. 2·03 A.	Normal 147·3 V. 2·49 A.	Normal 146·4 V. 2·49 A.	Normal 141·5 V. 3·49 A.
7082 } 6907 }	—	—	5·7	9·7
6234 } 6149 } 6124 } 6073 }	—	—	2·2	5·3
5790 } 5770 }	68·7	88·4	95·0	176·0
5461	73·4	91·0	98·9	161·0
4916	2·2	2·0	2·2	3·5
4358 } 4339 }	67·9	83·6	83·7	135·0
4078 } 4047 } 3984 }	33·1	41·3	46·0	72·0
3906	—	0·9	1·3	4·7
3704 } 3663 } 3655 } 3650 }	90·3	116·0	134·0	219·5
3342	5·9	8·6	10·8	17·7
3132 } 3126 }	56·7	67·4	91·1	140·3
3022	18·2	25·1	39·2	69·0
2967	11·5	13·6	21·1	32·7
2926	—	1·2	3·6	6·8
2894	3·6	4·9	8·3	11·4
2804	5·2	6·5	14·1	21·2
2753	—	1·4	4·6	7·2
2699	2·5	3·6	6·1	13·5
2655 } 2654 } 2652 } 2640 }	12·0	16·8	30·6	53·3
2603	—	—	4·4	7·5
2576	2·5	2·6	7·2	14·0
2537 } 2535 }	18·1	24·0	50·9	76·4
2482	4·1	6·0	12·9	20·5
2464	—	—	3·1	—
2447	—	—	3·1	—
2399	2·0	2·9	7·7	11·8
2378	1·9	3·0	7·5	8·4
2353	—	—	5·2	6·4
2323	—	—	3·2	—
2302	—	—	6·1	—
Total	480	611	809	1295
Total for λ 3132 and shorter wave-lengths	138	179	330	500

535.338.4 : 546.881

THE BAND SPECTRUM OF VANADIUM OXIDE

By P. C. MAHANTI, M.Sc.

Communicated by Prof. P. N. Ghosh, January 12, 1935. *Read in title March* 15, 1935.

ABSTRACT. The spectrum of VO has been photographed under high dispersion. Experimental evidence confirming that the emitting molecule is VO has been secured. The vibrational analysis of the band system has been extended to $v' = 8$, and approximate values of the vibrational constants have been calculated from the new band-head data. The rotational structure-analysis of the bands (0, 1), (0, 0) and (1, 0) shows the presence of two R and two P branches with a short Q branch. The rotational constants of the molecule have been evaluated. It is suggested that the band system is due to a $^2\Delta \rightarrow {}^2\Delta$ transition.

§ 1. INTRODUCTION

The spectrum of vanadium oxide, VO, consists of well-marked red-degrading bands which extend from violet to far red. As early as 1895 Demarçay[1] first observed them in the spark through a solution of vanadium fluoride. But the wave-length data of only a few of their heads were recorded by the early investigators[2]. Using low dispersion, Ferguson[3] has recently measured a large number of these bands.

The vibrational quantum-analysis of these bands was first undertaken by Mecke[4], who had identified only four heads, viz. (1, 0), (0, 0), (0, 1) and (0, 2) from the old data. Ferguson has included as many as thirty-one bands in the system. This enabled him to calculate approximate values of the vibrational constants of the molecule. He has published, however, no photograph of his spectrum.

The main object of the present investigation is to make a rotational structure-analysis of the bands. Of the band spectra known so far to be associated with the oxides of the elements of the transition groups, a structure-analysis has been made only in the case of the blue-green bands of titanium oxide and it might be interesting to make such a study for those of vanadium oxide. For this purpose, first- and second-order spectrograms taken with a 21-ft. concave grating have been utilized. In addition to this, photographs taken with a Hilger E. 1 prism spectrograph, of the Littrow type, with interchangeable quartz and glass optical systems, revealed the presence of a number of bands which have not been recorded previously. The new data of wave-lengths obtained for the band heads have been used to calculate the values of the vibrational constants, which do not differ appreciably from those of Ferguson.

§ 2. THE IDENTIFICATION OF THE EMITTER

The fact that the same band spectrum is emitted whether vanadium or its various salts are used in the core of the carbon arc in air, leads one to attribute it to the oxide of the metal but does not exclude the possibility of its being due to the hydride VH or the metal molecule V_2 itself. The rotational structure-analysis of the bands definitely rules out the hydride as the probable emitter, but some doubt is left as to whether V_2 might not be the molecule concerned. It was, therefore, considered desirable to obtain further experimental evidence regarding the identity of the emitter of the spectrum. Accordingly a water-cooled enclosed arc was used. The electrodes were of carbon, the lower one being cored to receive the metal or its salt. The arc could be satisfactorily maintained in different gases under varying pressures. It was found that the spectrum was emitted only in an atmosphere of either oxygen or air, while it was completely quenched when hydrogen or nitrogen was introduced into the arc chamber. This shows that the presence of oxygen is necessary to produce the bands and it may therefore be concluded that vanadium oxide, VO, is the emitter of the band spectrum in question.

§ 3. EXPERIMENTAL

The flame surrounding a carbon arc whose lower electrode contained metallic vanadium or vanadium salts was used as the source of radiation. Various salts such as vanadium chloride, vanadium phosphate, ammonium vanadate and vanadic acid have been used. The arc was operated at a current-density of 4 to 5 A. from 220-V. d.-c. mains.

For a preliminary survey spectrograms were obtained with the help of a Hilger E. 1 prism spectrograph. Ilford special rapid panchromatic plates were used. With an exposure of about 20 to 30 minutes, the bands were very well developed on the plates in the region extending from $\lambda 4400$ to about $\lambda 7100$. For photographing the bands beyond $\lambda 7100$ dicyanine and kryptocyanine plates were used. The time of exposure was about 2 hours. The bands were then found to extend as far as $\lambda 8650$. In the long wave-length region they were also photographed in the first order of a 15-ft. concave grating having 15,000 lines per inch.

For measuring structure lines of the bands, photographs were taken in the first and second orders of a 21-ft. concave grating set up in Paschen mounting and having 30,000 lines per inch with a 6-inch ruled surface. In the first order, an exposure of about 3 hours was sufficient to get the lines well developed for measurements. But in the second order the time of exposure was as long as 8 hours. Even then the lines, although just intense enough for measurement, were not sufficiently strong for reproduction.

Measurements of band heads and structure lines were made on several of the plates taken with the prism and grating spectrographs, figure 1. The dispersions

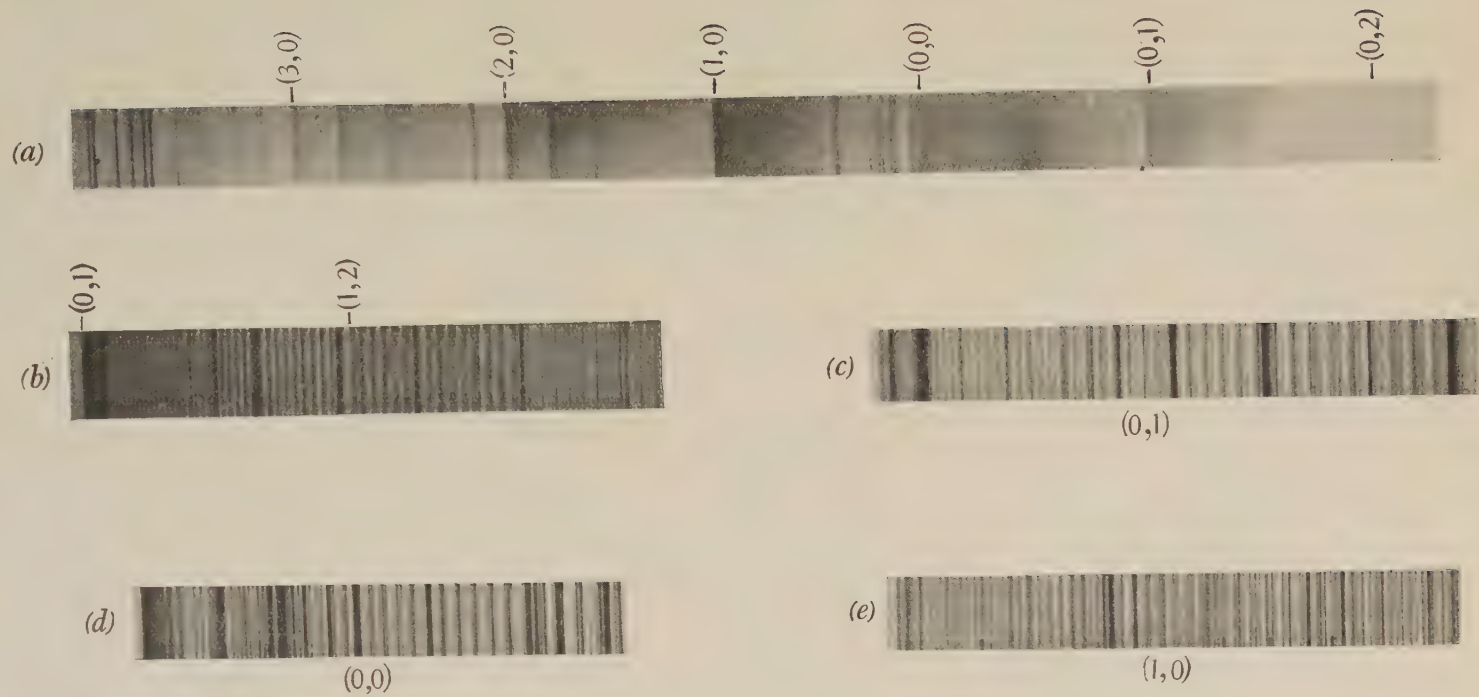

Figure 1. VO bands: (*a*) Hilger E. 1 quartz spectrograph; (*b*) 15-ft. grating, first order; (*c, d, e*) 21-ft. grating, first order.

given by these instruments were as follows:

Prism spectrograph, E. 1

with quartz optical system, 16 A. mm. at λ4400 to 55 A. mm. at λ7100,

with glass optical system, 6 A. mm. at λ4400 to 36 A. mm. at λ7600;

15-ft. grating spectrograph, 3·55 A./mm. in the first order;

21-ft. grating spectrograph, 0·62 A./mm. in the second order.

For standards of comparison, iron arc, neon and hydrogen lines were used for different regions of the spectrum. Measurements were made in the usual way with a Gaertner comparator.

Particulars of the observed bands are included in table 1, which indicates wave-lengths in air, wave-numbers *in vacuo* and relative intensities of the band heads. The data for the structure lines of (0, 1), (0, 0) and (1, 0) bands are given respectively in tables 2, 3 and 4.

§ 4. VIBRATIONAL ANALYSIS

As has already been stated, it was Mecke who initiated the vibrational quantum-analysis of the bands. From the data of Eder and Valenta, he assigned the heads at $\lambda\lambda$5470, 5737, 6087 and 6478 respectively to (1, 0), (0, 0), (0, 1) and (0, 2) bands of the system. In addition to these, Ferguson included as many as twenty-seven bands, which are fairly intense. He evaluated the following vibrational constants in cm^{-1}:

$$\nu_e = 17498{\cdot}8,\quad \omega_e' = 864{\cdot}8,\quad \omega_e'x_e' = 5{\cdot}70,\quad \omega_e'' = 1012{\cdot}3,\quad \text{and}\quad \omega_e''x_e'' = 5{\cdot}27.$$

In the present investigation, a large number of new heads have been incorporated in the system. For comparison, Ferguson's wave-number data have been included in table 1 together with the assignment of v', v'' values to each band head.

Assuming that the heads are very close to the band origins, the equation derived for the R heads is

$$\nu = 17501{\cdot}3 + [863{\cdot}5\,(v' + \tfrac{1}{2}) - 5{\cdot}4\,(v' + \tfrac{1}{2})^2] - [1012{\cdot}7\,(v'' + \tfrac{1}{2}) - 4{\cdot}9\,(v'' + \tfrac{1}{2})^2].$$

The distribution of relative intensities of the bands in the system follows a typical wide Condon parabola.

It may here be noted that in addition to the bands included in the present system, Ferguson measured forty-five heads which he thinks may also be due to VO. They lie in the far red region of the spectrum and probably extend still towards the higher wave-length side. These bands could neither be fitted into an independent system nor incorporated into the existing one. Fourteen of them were, however, formed into four sequences and their first differences indicate that they might be related to the band system under consideration. In the present investigation these bands have not been obtained owing probably to the want of sensitiveness of the plates used.

Table 1

v', v''	λ in air and intensity	ν *in vacuo*		v', v''	λ in air and intensity	ν *in vacuo*	
		Author	Ferguson			Author	Ferguson
6, 0	4466·4 (0)	22383·1	—	2, 2	5837·3 (4)	17126·5	17125
7, 1	4510·1 (1)	22166·3	—	4, 4	5942·5 (1)	16823·3	—
8, 2	4554·1 (1)	21952·1	—	5, 5	5997·6 (1)	16668·7	—
5, 0	4632·7 (2)	21579·7	—	0, 1	6086·4 (8)	16425·4	16428
6, 1	4676·8 (2)	21376·2	—	1, 2	6139·1 (3)	16284·5	—
7, 2	4721·2 (2)	21175·1	—	2, 3	6191·6 (2)	16146·5	—
8, 3	4767·5 (1)	20969·1	—	3, 4	6247·2 (1)	16002·7	—
4, 0	4813·5 (3)	20769·1	20773	4, 5	6303·3 (1)	15860·3	—
5, 1	4858·5 (4)	20576·7	20578	5, 6	6360·4 (3)	15717·9	—
6, 2	4904·2 (4)	20385·0	20383	6, 7	6418·5 (1)	15575·7	—
7, 3	4951·2 (2)	20191·5	20191	0, 2	6477·8 (6)	15433·1	15433
8, 4	4999·1 (2)	19998·0	—	1, 3	6532·8 (6)	15303·2	15306
3, 0	5010·5 (4)	19952·5	19950	2, 4	6588·9 (3)	15172·9	15174
4, 1	5057·3 (4)	19767·9	19768	3, 5	6646·4 (2)	15041·6	—
5, 2	5104·1 (3)	19586·7	19586	4, 6	6706·0 (1)	14907·9	—
6, 3	5152·5 (3)	19402·7	—	5, 7	6766·2 (1)	14775·3	—
7, 4	5201·4 (2)	19220·3	—	6, 8	6827·6 (1)	14642·4	—
2, 0	5228·2 (6)	19121·7	19121	0, 3	6919·0 (4)	14449·0	14454
3, 1	5275·8 (6)	18949·2	18951	1, 4	6976·2 (4)	14330·5	14334
4, 2	5324·5 (6)	18775·9	18779	2, 5	7035·2 (3)	14210·3	14212
5, 3	5373·3 (2)	18605·4	—	3, 6	7095·6 (3)	14089·4	14098
6, 4	5425·1 (1)	18427·7	—	4, 7	—	—	13984
1, 0	5469·3 (9)	18278·8	18279	0, 4	7418·2 (3)	13476·6	13479
2, 1	5517·3 (5)	18119·8	18123	1, 5	7477·0 (2)	13370·7	13376
3, 2	5567·7 (4)	17955·8	—	2, 6	7538·2 (1)	13262·1	13270
4, 3	5618·0 (3)	17795·0	—	3, 7	—	—	13166
5, 4	5669·9 (2)	17632·1	—	0, 5	7986·0 (2)	12518·5	12522
6, 5	5723·8 (1)	17466·1	—	1, 6	—	—	12426
0, 0	5736·7 (10)	17426·9	17425	0, 6	8643·4 (2)	11566·3	11571
1, 1	5786·4 (1)	17277·1	—	1, 7	—	—	11489

§ 5. ROTATIONAL ANALYSIS

The strongest bands in the system, namely (1, 0), (0, 0) and (0, 1), were chosen for a study of rotational structure. Under high dispersion they show two heads very close to one another, although the resolution is incomplete in their neighbourhood. As one proceeds a little farther from the second head, two series of lines can be clearly followed. Each member of these series in its turn breaks up into two components giving rise to an extended set of four series of lines. *A priori* this leads one to think that the four series are probably due to R_1, R_2, P_1 and P_2 branches, although the individual series could not be assigned to any definite branch. As a first step towards the identification of the different series it was thought necessary to form all possible combinations between the members of any two series for each of the bands under consideration. Different sets of frequency-differences were thus obtained. With a view to selecting from them the proper combination differences between the lines of an R and a P branch, we next proceeded to ascertain probable values of $\Delta_2 T$. We had thus to assume first a value of B_0 which involves a knowledge of r_0 for the vanadium-oxide molecule. From Morse's relation, $\omega_0 r_0^3 \doteq$ a constant,

one can calculate the value of r_0 for a molecule whose ω_0 is known, provided the magnitude of the constant can be properly chosen. The value of this constant was secured from the data of Christy[5] for the blue-green bands of titanium oxide. r_0 being known, B_0 was calculated and finally the expected values of $\Delta_2 T$ were obtained. With these values in mind, the frequency differences obtained from any two series of the (0, 0) band were compared with those from any two series of the (0, 1) band. When two sets of approximately equal values of $\Delta_2 T$, one from each band, were obtained, then the pair of series of the (0, 0) band were shifted by two units with respect to each other and were compared with an arbitrary pair of series of the (1, 0) band. It was found, however, that no combination relations could be satisfied except for a few members of the series. The above procedure was repeated for several other values of B_0 and thus of $\Delta_2 T$ in the neighbourhood of the one already tried. But each of these trials proved futile. This failure indicated that the values of B_0 tried were not the true values, and consequently the true values of $\Delta_2 T$ for the band lines could not be obtained. This supposition seems to be justified from the fact that, as Christy has remarked, the value of r_0 for the titanium-oxide molecule is decidedly small and is much less than the minimum value predicted by Birge. One may therefore expect that the value of $\omega_0 r_0^3$ is probably higher than that on which the above approximate values of B_0 are based. Hence the next procedure consisted in finding out whether for any sets of frequency-differences, irrespective of the magnitude of B_0, the combination relation could be satisfied between the three bands for any two of the four series of lines. After repeated trials pairs of such series were found for each of the bands, and in each pair the identification of R and P series was consequently ascertained and so also their J numbering. This helped us in identifying the two components of R and P branches. But it was difficult to decide which of them is to be associated with R_1, R_2 and P_1, P_2 series. It was then found that of the two series of lines which emanate a little distance away from the second head, one is a component of the R branch while the other is formed from the superposition of the second component of the R branch and of one component of the P branch. When each of these series is extrapolated towards the head, only one of them is found to form the first head while the other coalesces into it before reaching the second head. This shows evidently that the second head is not due to an R branch, and its head-like appearance may be attributed to the condensation of lines of a Q branch. It may further be noted that in band systems due to non-hydride molecules, R_1 and R_2 heads are separated only in cases where either the heads are formed by R-branch lines having high values of K or where the spin doubling is large. None of these criteria is fulfilled by the present analysis. On the other hand a further close inspection of the plates did not reveal the existence of a definite series which may be assigned to a Q branch. It is, therefore, probable that the Q branch is very short although it begins with appreciable intensity. It should be noted, however, that the superposition of the lines of the returning R branch also adds to the apparent intensity of the second head. From the values of B_v' and B_v'' evaluated from the analysis of the bands, the wave-numbers of the first few lines of a Q branch were calculated

and they were found to lie very close to one another. It is quite probable that they would present a head-like appearance under the dispersion used. Besides this, the intervals between the first and second heads of (0, 1), (0, 0) and (1, 0) bands also satisfy the criterion for the identification of Q heads as they are respectively equal to 2·83, 2·64 and 2·41 cm.$^{-1}$

In tables 2, 3 and 4, wave-number data of the structure lines with their K numbering are given. They also include the mean values of the rotational term-differences for the upper and lower states, defined as follows.

In the upper state,

$$\Delta_2T_1'(J)=R_1(J)-P_1(J), \text{ for } J=K+\tfrac{1}{2},$$

and

$$\Delta_2T_2'(J)=R_2(J)-P_2(J), \text{ for } J=K-\tfrac{1}{2},$$

so that,

$$\Delta_2T'(K)=\tfrac{1}{2}\{\Delta_2T_1'(J)+\Delta_2T_2'(J)\}.$$

While in the lower state,

$$\Delta_2T_1''(J)=R_1(J-1)-P_1(J+1), \text{ for } J=K+\tfrac{1}{2},$$

and

$$\Delta_2T_2''(J)=R_2(J-1)-P_2(J+1), \text{ for } J=K-\tfrac{1}{2},$$

so that,

$$\Delta_2T''(K)=\tfrac{1}{2}\{\Delta_2T_1''(J)+\Delta_2T_2''(J)\}.$$

The combination differences, $\Delta_2T(K)$, can be expressed thus:

$$\Delta_2T(K)=4B_v(K+\tfrac{1}{2})+8D_v(K+\tfrac{1}{2})(K^2+K+1),$$

where B_v and D_v depend upon v.

§ 6. ROTATIONAL CONSTANTS

To calculate B_v and D_v corresponding to a given vibrational state the mean values of the combination differences $\Delta_2T(K)$ have been taken in cases where more than one datum were available for a particular pair of rotational levels. Then by the method of successive approximation the following constants were evaluated:

$B_e'=0{\cdot}33485$ cm.$^{-1}$	$B_e''=0{\cdot}38760$ cm.$^{-1}$
$B_0'=0{\cdot}33350$	$B_0''=0{\cdot}38640$
$B_1'=0{\cdot}33080$	$B_1''=0{\cdot}38400$
$\alpha'=0{\cdot}0027$	$\alpha''=0{\cdot}0024$
$D_e'\doteq D_v'=2{\cdot}01\times10^{-7}$	$D_e''\doteq D_v''=2{\cdot}27\times10^{-7}$
$r_e'=2{\cdot}029\times10^{-8}$ cm.	$r_e''=1{\cdot}886\times10^{-8}$ cm.
$I_e'=82{\cdot}67\times10^{-40}$ gm.cm.^{2}	$I_e''=71{\cdot}42\times10^{-40}$ gm.cm.^{2}

With the values of the molecular constants now available one can check the correctness of the rotational analysis of the bands as follows. On substitution of the values of B_e and D_e in the theoretical relation

$$\omega_e^2=-4B_e^3/D_e,$$

it is found that $\omega_e'=864{\cdot}4$ cm.$^{-1}$ and $\omega_e''=1012{\cdot}9$ cm.$^{-1}$ These values are in sufficient close agreement with those obtained from the vibrational analysis of the bands.

Table 2. (1, 0) band, λλ5469·30 (*R*), 5470·02 (*Q*)

K''	R	P	$\Delta_2T'(K)$ $v'=1$	$\Delta_2T''(K)$ $v''=0$	K''	R	P	$\Delta_2T'(K)$ $v'=1$	$\Delta_2T''($ $v''=$
4	18278·81	18270·70	—	—	35	18229·35	18181·87	47·28	55·1
5	—	69·49	—	—		27·59	80·52		
6	—	68·19	—	—	36	26·06	77·28	48·59	56·5
7	—	66·82	—	—		24·23	75·82		
8	—	65·32	—	—	37	22·67	72·85	49·78	58·0
9	—	63·68	—	—		20·78	71·03		
10	—	61·98	—	—	38	19·18	68·13	51·06	59·5
11	—	60·18	—	—		17·22	66·15		
12	—	58·25	—	—	39	15·57	63·24	52·33	61·0
13	—	56·18	—	—		13·54	61·20		
14	—	53·98	—	—	40	11·85	58·19	53·64	62·5
15	—	51·65	—	—		09·73	56·12		
16	18270·70	49·05	21·42	—	41	08·03	52·95	54·96	64·2
	70·23					05·81	50·97		
17	69·49	46·32	22·88	26·94	42	04·09	47·61	56·42	65·9
	68·92					01·80	45·44		
18	68·19	43·52	24·35	28·50	43	00·05	42·08	57·90	67·3
	67·56					18197·69	39·87		
19	66·82	40·79	25·73	30·11	44	95·90	36·85	59·08	68·7
	66·05	40·62				93·49	34·38		
20	65·32	37·90	27·12	31·73	45	91·73	31·58	60·28	70·3
	64·45	37·63				89·18	28·76		
21	63·68	34·87	28·53	33·33	46	87·56	25·70	61·83	71·9
	62·78	34·54				84·75	22·94		
22	61·98	31·77	29·95	34·90	47	82·33	19·98	63·22	73·5
	61·02	31·34				80·22	17·13		
23	60·18	28·59	31·33	36·51	48	79·09	14·17	64·70	75·1
	59·15	28·08				75·59	11·12		
24	58·15	25·29	32·71	38·14	49	74·67	08·30	66·11	76·8
	57·15	24·70				70·87	05·02		
25	56·18	21·87	34·07	39·75	50	70·21	02·13	67·66	78·5
	55·01	21·17				66·05	18098·82		
26	53·98	18·35	35·41	41·25	51	—	95·87	—	80·1
	52·74	17·56					92·60		
27	51·65	14·74	36·67	42·78	52	—	89·75	—	—
	50·38	13·94					86·25		
28	49·22	10·99	37·99	44·29	53	—	83·41	—	—
	47·92	10·18					80·07		
29	46·72	07·14	39·33	45·84	54	—	77·06	—	—
	45·38	06·31					73·47		
30	44·12	03·16	40·69	47·40	55	—	70·72	—	—
	42·72	02·30					67·07		
31	41·42	18199·12	42·01	48·96	56	—	64·29	—	—
	39·90	98·19					60·57		
32	38·56	94·98	43·32	50·47	57	—	57·93	—	—
	37·00	93·95					53·88		
33	35·63	90·77	44·62	52·03	58	—	51·44	—	—
	34·00	89·61							
34	32·54	86·40	45·94	53·62					
	30·84	85·11							

Table 3. (0, 0) band, $\lambda\lambda$ 5735·66 (R), 5737·53 (Q)

R	P	$\Delta_2T'(K)$ $v'=1$	$\Delta_2T''(K)$ $v''=0$	K''	R	P	$\Delta_2T'(K)$ $v'=1$	$\Delta_2T''(K)$ $v''=0$
17426·92	17417·85	—	—	42	17355·35	17299·25	56·30	65·21
—	16·69	—	—		54·32	97·81		
—	15·39	—	—	43	51·46	94·10	57·52	66·68
—	13·99	—	—		50·44	92·75		
—	12·48	—	—	44	47·52	88·84	58·84	68·20
—	10·87	—	—		46·46	87·46		
—	09·11	—	—	45	43·48	83·48	60·17	69·76
—	05·38	—	—		42·37	82·02		
—	03·32	—	—	46	39·30	78·02	61·51	71·32
—	01·14	—	—		38·19	76·44		
—	17398·87	—	—	47	35·03	72·41	62·84	72·94
17418·45	96·48	21·97	—		33·86	70·80		
17·33	94·00	23·33	27·08	48	30·73	66·53	64·27	74·64
16·06	91·37	24·69	28·69		29·41	65·07		
14·69	88·64	26·05	30·14	49	26·29	60·36	65·79	76·23
13·21	85·92	27·29	31·81		24·88	59·25		
12·48	83·47	28·81	33·35	50	—	54·16	66·90	77·88
11·60	82·99				20·23	53·33		
10·87	80·54	30·13	34·85	51	—	48·12	68·23	79·07
09·90	79·97				15·52	47·29		
09·11	71·49	31·45	36·37	52	—	41·99	69·53	80·63
08·17	76·89				10·69	41·16		
07·32	74·32	32·79	37·98	53	—	35·75	70·85	82·16
06·29	73·71				05·74	34·89		
05·38	70·97	34·18	39·55	54	—	29·48	72·18	83·68
04·32	70·36				00·71	28·53		
03·32	67·62	35·50	41·14	55	—	23·13	73·47	85·20
02·20	66·89				17295·53	22·06		
01·14	64·09	36·85	42·68	56	—	16·66	74·76	86·69
17399·99	63·33				90·27	15·51		
98·87	60·47	38·20	44·18	57	—	10·20	76·08	88·24
97·69	59·69				84·92	08·84		
96·48	56·79	39·51	45·68	58	—	03·77	77·45	89·81
95·30	55·98				79·48	02·03		
94·00	52·97	40·79	47·14	59	—	17197·38	78·79	91·41
92·79	52·24				73·90	95·11		
91·37	49·08	42·03	48·61	60	—	91·32	80·13	92·98
90·19	48·42				68·20	88·07		
88·64	45·11	43·27	50·10	61	—	84·48	82·83	95·95
87·46	44·45				62·42	80·92		
85·80	41·05	44·52	51·59	62	—	77·73	84·12	97·48
84·62	40·32				56·55	73·72		
82·83	36·84	45·79	53·11	63	—	71·45	85·45	—
81·66	36·08				50·59	66·47		
79·66	32·48	47·02	54·63	64	—	65·23	—	—
78·58	31·72				44·52	59·07		
76·52	28·00	48·35	56·12	65	38·27	—	—	—
75·41	27·22			66	32·01	—	—	—
73·23	23·44	49·68	57·67	67	25·62	—	—	—
72·14	22·57			68	19·13	—	—	—
69·85	18·79	51·02	59·20	69	12·56	—	—	—
68·79	17·80			70	06·26	—	—	—
66·38	14·05	52·37	60·76	71	17199·78	—	—	—
65·32	12·91			72	93·45	—	—	—
62·82	09·22	53·75	62·32	73	86·89	—	—	—
61·80	07·90			74	80·33	—	—	—
59·15	04·28	55·10	63·78					
58·12	02·78							

Table 4. (0, 1) band, $\lambda\lambda$6086·44 (R), 6087·49 (Q)

K''	R	P	$\Delta_2T'(K)$ $v'=0$	$\Delta_2T''(K)$ $v''=1$
3	—	16417·90	—	—
4	—	16·79	—	—
5	—	15·56	—	—
6	16425·43	14·21	—	—
7	—	12·78	—	—
8	—	11·30	—	—
9	—	09·76	—	—
10	—	08·12	—	—
11	—	06·37	—	—
12	—	04·54	—	—
13	—	02·63	—	—
14	—	00·56	—	—
15	—	16398·38	—	—
16	16418·52	96·12	22·09	—
	17·90			
17	17·42	93·78	23·33	26·90
	16·79			
18	16·18	91·31	24·56	28·63
	15·56			
19	14·80	88·48	26·03	30·11
	14·21			
20	13·37	85·76	27·32	31·56
	12·78			
21	11·89	82·95	28·88	33·27
	11·30	82·47		
22	10·36	80·08	30·26	34·76
	09·76	79·52		
23	08·79	77·15	31·62	36·29
	08·12	76·51		
24	07·12	74·10	32·97	37·85
	06·37	73·43		
25	05·37	70·96	34·35	39·39
	04·54	70·24		
26	03·46	67·72	35·69	40·94
	02·63	66·99		
27	01·47	64·39	37·00	42·47
	00·56	63·64		
28	16399·37	60·98	38·30	43·99
	98·38	60·16		
29	97·20	57·46	39·64	45·50
	96·12	56·58		
30	94·91	53·84	40·97	47·00
	93·78	52·91		
31	92·52	50·13	42·25	48·53
	91·31	49·19		
32	90·07	46·31	43·61	50·04
	88·78	45·32		
33	87·49	42·38	44·96	51·59
	86·17	41·36		
34	84·78	38·37	46·28	53·09
	83·46	37·30		
35	82·01	34·31	47·58	54·58
	80·64	33·17		
36	79·12	30·15	48·86	56·09
	77·69	28·93		
37	76·14	25·86	50·15	57·59
	74·63	24·61		
38	73·05	21·46	51·45	59·09
	71·47	20·16		
39	69·86	16·96	52·75	60·56
	68·23	16·53		
40	66·62	12·40	54·06	62·05
	64·90	11·00		
41	63·27	07·69	55·39	63·58
	61·50	06·29		
42	16359·82	16302·90	56·77	65·
	58·08	01·45		
43	56·25	16298·02	58·13	66·
	54·54	96·50		
44	52·56	93·05	59·44	68·
	50·85	91·48		
45	48·82	87·96	60·76	69·
	47·03	86·36		
46	44·97	82·78	62·07	71·
	43·10	81·14		
47	40·99	77·48	63·38	72·
	39·09	75·83		
48	36·93	72·05	64·73	74·
	35·01	70·43		
49	32·79	66·52	66·08	75·
	30·82	64·93		
50	28·55	60·88	67·42	77·
	26·05	59·32		
51	24·21	55·14	68·76	78·
	22·07	53·61		
52	19·76	49·86	69·83	80·
	17·57	47·80		
53	15·20	44·00	71·11	81·
	12·97	41·94		
54	10·55	38·04	72·42	83·
	08·26	35·93		
55	05·81	32·00	73·70	84·
	03·44	29·84		
56	00·97	25·86	75·00	86·
	16298·55	23·65		
57	96·03	19·62	76·30	87·
	93·58	17·38		
58	90·98	13·28	77·59	89·
	88·49	11·00		
59	85·86	06·87	78·88	—
	83·31	04·53		
60	80·61	—	—	—
	78·04			
61	75·30	—	—	—
	72·63			
62	69·88	—	—	—
	67·20			
63	64·37	—	—	—
	61·49			
64	58·74	—	—	—
	55·83			
65	53·03	—	—	—
	50·23			
66	47·25	—	—	—
	44·40			
67	41·36	—	—	—
	38·46			
68	35·40	—	—	—
	32·45			
69	29·37	—	—	—
	26·36			
70	—	—	—	—
	20·18			
71	—	—	—	—
	13·92			
72	—	—	—	—
	07·60			

A further check is afforded by Birge's rule:

$$2x_e B_e/\alpha = 1{\cdot}4 \pm 0{\cdot}2.$$

For these bands substitution of the proper values shows that

$$2x_e' B_e'/\alpha' = 1{\cdot}55 \quad \text{and} \quad 2x_e'' B_e''/\alpha'' = 1{\cdot}56.$$

It should be noted that the nuclear separation of VO thus obtained is in fair conformity with the value predicted by Mecke[6], who plotted the nuclear separation of all known hydrides of various elements against the respective atomic number of the element. He found that r_e of the hydrides of the elements between He and Ne, Ne and A, A and Kr lie respectively on three widely spaced lines. The nuclear separation of vanadium hydride, according to this graph, should be about $1{\cdot}87 \times 10^{-8}$ cm. The value of r_e for vanadium oxide as estimated by comparing the values of the nuclear separation of the hydrides with those of the oxides is estimated to lie between 1·85 and $2{\cdot}35 \times 10^{-8}$ cm.

§ 7. ELECTRONIC TRANSITION

The analysis reveals that each band consists of two R and two P branches and is, therefore, due to a transition between two similar doublet states. Even at high rotational quantum numbers none of these branches shows any splitting that could be attributed to Λ-type doubling. Thus the possibility of a $^2\Pi \rightarrow {}^2\Pi$ transition is excluded. Although we cannot ascertain with certainty the number of missing lines in the P and R series owing to the superposition of the branches and want of resolution in the neighbourhood of the origins of the bands, still the presence of a short and strong Q branch rules out $^2\Sigma \rightarrow {}^2\Sigma$[7] leaving $^2\Delta \rightarrow {}^2\Delta$ as the only probable transition concerned.

Further, such a transition is to be expected from the consideration of the molecular electronic states. Assuming that the lower electronic state of VO is derived from a normal V atom and a normal O atom respectively in $3d^3 4s^2 ({}^4F)$ and $2s^2 2p^4 ({}^3P)$ states, the possible molecular states are only those with $\Lambda = 1, 3, 4$ and $S = \frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}$. Hence the probability of a $^2\Sigma$ or $^2\Pi$ as the ground state of the molecule is excluded. This leads one to suggest that $^2\Delta \rightarrow {}^2\Delta$ is the transition concerned in the emission of the band system, although the criteria of missing lines and intensity relation between the branches for low rotational quantum numbers would have settled this question more definitely.

8. POTENTIAL-ENERGY CURVES AND PRODUCTS OF DISSOCIATION

The actual dissociation energies corresponding to the upper and lower electronic states of the molecule are calculated from the relation

$$\mathbf{D} = \omega_e^2/4x_e\omega_e - \tfrac{1}{2}\omega_e,$$

and it is found that $\mathbf{D}' = 4{\cdot}20$ volts and $\mathbf{D}'' = 6{\cdot}38$ volts. Now by means of the relation given below we can ascertain the electronic states of one of the products

of dissociation by calculating E_{atom} from the observed $E_{mol.}$ and the values of $\mathbf{D}'$ and $\mathbf{D}''$. Assuming as is usually done that the oxygen atom remains in its normal state (^3P) in both the excited and unexcited states of the molecule, the electronic state of vanadium atom when dissociated in the excited state can be derived. We know that

$$E_{mol.}+\mathbf{D}'=\mathbf{D}''+E_{atom},$$

i.e.

$$E_{atom}=E_{mol.}+(\mathbf{D}'-\mathbf{D}'').$$

In the band system under consideration, $E_{mol.}$ corresponding to the origin of the (0, 0) band is 2·15 V., so that $E_{atom}=-0{\cdot}03$ V. Considering the limits of extrapolation error in the values of $\mathbf{D}'$ and $\mathbf{D}''$, we may take E_{atom} as 0. It is therefore clear that both the $^2\Delta$ states of VO dissociate into the same products, namely, the unexcited atoms of vanadium and oxygen, V (^4F)+O (^3P).

Similar conclusions have been drawn by Mulliken [8] in the case of N_2^- negative system involving a $^2\Sigma\rightarrow{}^2\Sigma$ transition and few other isoelectronic diatomic molecules. For N_2^- Mulliken also predicts the existence of a band system, probably lying in the far red, from an analogy with these molecules. In the case of VO one is led to suspect that the bands recorded by Ferguson in the far-red region of the spectrum might be a part of another system for the molecule.

It is interesting to note that for the oxides of the elements of the first transition group, E_{atom} calculated from the data of the blue bands (system I) of ScO, of the blue-green bands of TiO, and of the band systems known for CrO and MnO, is found to be negligibly small in each case. These values are shown in table 5.

Table 5

	$E_{mol.}$	$\mathbf{D}'$	$\mathbf{D}''$	E_{atom}
ScO	2·5	4·6	7·5	−0·4
TiO	2·4	4·8	6·9	+0·3
VO	2·2	4·2	6·4	0·0
CrO	2·0	1·9	3·8	+0·1
MnO	2·2	1·7	4·4	−0·5

With the data now available for ω_e, r_e and $\mathbf{D}_e$ it is possible to construct, after Morse, the $U(r)$ curves for the excited and unexcited states of the vanadium oxide molecule. These curves are given in figure 2. They meet one another for values of r much greater than r_e and represent the case of a pair of molecular states which dissociate into the same atomic states.

§ 9. ACKNOWLEDGMENTS

The author wishes to express sincere thanks to Prof. P. N. Ghosh for his encouragement during the course of the investigation and to Prof. R. W. Wood for kindly supplying the 21-ft. grating without which the present work could not have been carried out.

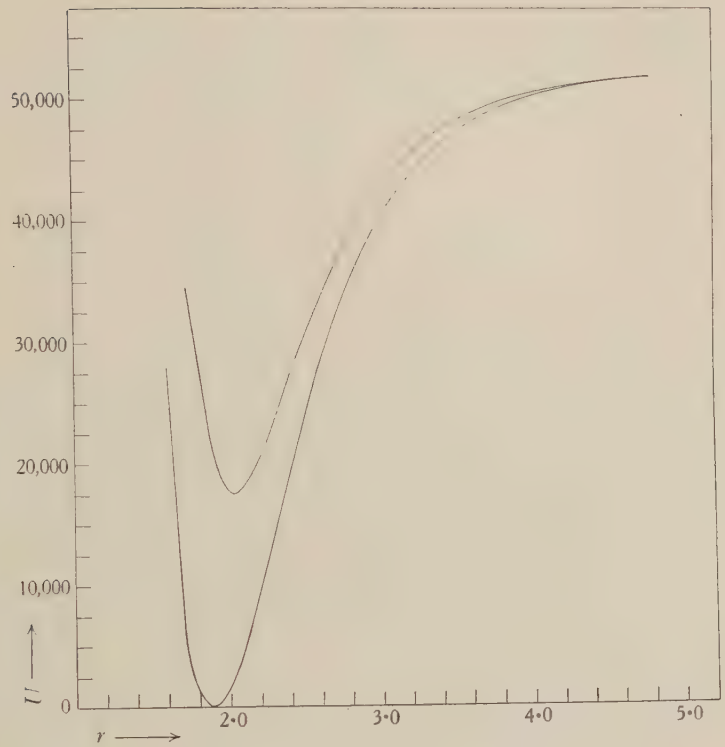

Figure 2. Curves relating U with r.

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NEW METHOD OF MEASURING THE TIME AND EFFICIENCY OF PHOTOGRAPHIC SHUTTERS*

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ABSTRACT. Apparatus is described for obtaining the curves relating area with time in photographic between-lens shutters. A set of separated and illuminated apertures fitted with neutral glass filters passing certain standard fractions of the light is imaged by a lens on film wrapped round a revolving drum, the shutter acting as a diaphragm for the lens. The film is thus exposed in bands along its length. An exposure is made, with the shutter set fully open, for one revolution of the drum. The above apertures are then replaced by a second set without neutral filters, each of these apertures fitting exactly between the spaces previously occupied by two apertures of the previous set. An instantaneous exposure of the shutter is then made during another revolution of the drum. During the whole of this exposure a time scale is impressed on the film by subsidiary apparatus. After development the points at which adjacent bands have the same density are found. These give the times at which the area of opening of the shutter was equal to the standard fractions of its full aperture. Various features of the apparatus are discussed, and particulars are given of the method of calibrating the neutral filters and of tests carried out on shutters for which curves relating area with time could be calculated.

§ 1. INTRODUCTION

THE ideal photographic shutter opens to its full aperture infinitely quickly, stays fully open for a predetermined period, and then closes infinitely quickly. If A is the area of the full aperture and T the time of opening, the total amount of light admitted by the shutter is proportional to AT. In actual fact a shutter takes some time to open and some time to close, and the total amount of light admitted is proportional to $\int_0^T a\,dt$, where a is the area open at a time t, measured from the commencement of opening, and T the total time from beginning to end of the exposure. If the shutter has a full aperture A, the quantity $\frac{1}{AT}\int_0^T a\,dt$ is termed the efficiency.

The first measurements of efficiency appear to have been made by Abney in 1892[1]. A more accurate method following the same principles was published in 1909[2] from the National Physical Laboratory. This gives a record of the length of a line, across the aperture of the shutter, which is visible at any instant during

* Communication H 544 from the Kodak Research Laboratories.

the exposure. By independent experiments is obtained the relation between the area of opening of the shutter and the length of line visible, which enables the relation between area of opening and time to be plotted for the shutter. One of these operations was eliminated in apparatus devised in the Kodak Research Laboratories[3] which gave a high-speed kinematographic record of the position of the shutter blades at short, equally-spaced intervals of time. For accurate estimation of the efficiency these methods require the measurement, with a planimeter or otherwise, of the area uncovered by the shutter blades at recorded instants.

The apparatus now to be described gives a photographic record of the time at which the area of the shutter uncovered by the blades amounts to certain fractions of the aperture when fully open; that is, it provides directly a certain number of points on the area-and-time curve of the shutter. It was built specifically for between-lens shutters with a full aperture of diameter not greater than 25 mm. and exposure times of from 1·0 to 0·004 sec.

§ 2. DESCRIPTION OF APPARATUS

An image of the incandescent ball P of a 500-candle-power pointolite lamp is formed by the condenser lens L_1 at the plane S of the shutter blades, figure 1. Just in front of the condenser lens is a diaphragm which may be rotated into either

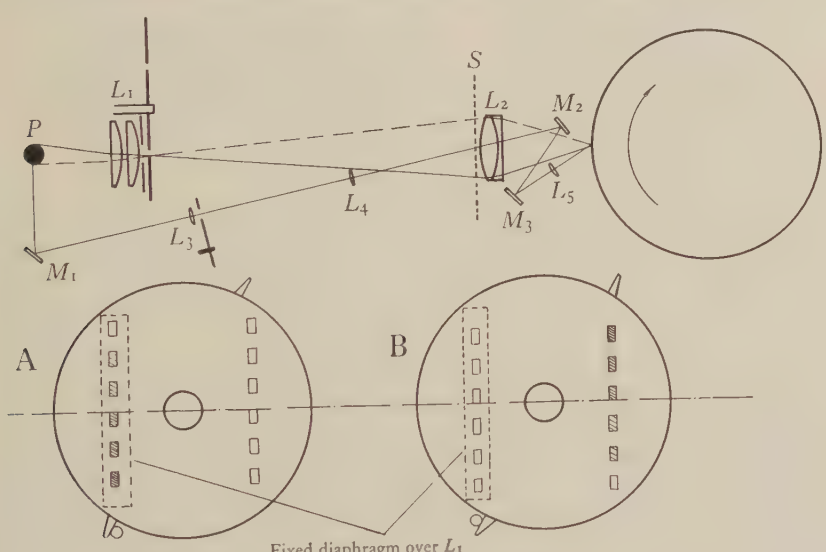

Figure 1. Diagram of apparatus.

of two positions. In one of these positions it forms a column of equal apertures at equal intervals, coming within the fixed rectangular aperture over the condenser lens indicated by the broken lines, figure 1 A. In the other position a second column of similar apertures fits exactly between the spaces previously occupied by the first set of apertures, figure 1 B. All but one of the apertures of the first set have

neutral glass filters fitted so that the transmissions of the apertures are 1·0, 0·9, 0·7, 0·5, 0·3 and 0·1 approximately. An image of the apertures is formed by the lens L_2, placed close to the plane S, on the surface of a strip of kinematograph film wrapped round a drum which can be steadily rotated.

An exposure is made to the first set of apertures for one revolution of the drum with the shutter under test open at full aperture. The film is thus, owing to its motion, exposed in bands corresponding to the image of the apertures at intensities 1·0, 0·9, 0·7, 0·5, 0·3 and 0·1 of the intensity transmitted by the shutter at full aperture; see figure 2*a*. Then the diaphragm in front of the condenser is rotated into the other position, and an exposure is made with the shutter set at the instantaneous exposure being measured. This results in another exposure in bands, corresponding to the image of the second set of apertures, figure 2*b*, but in this case the exposures in all the bands are the same but increase and then diminish in

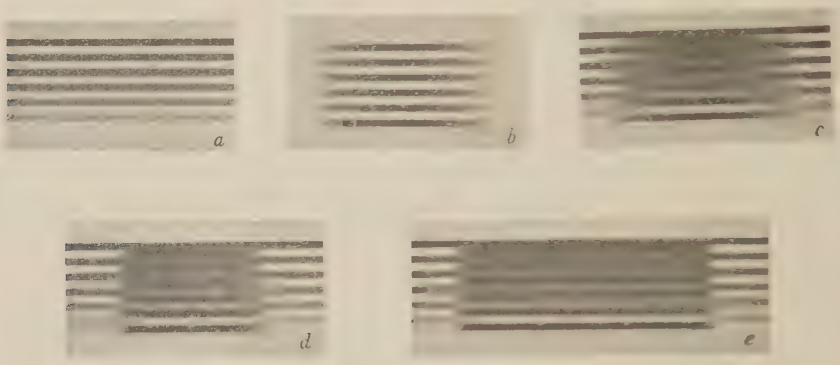

Figure 2. Examples of records.

intensity along the length of the film according to the area-and-time curve of the shutter. This second set of bands is, of course, interposed exactly between the first bands, figure 2*c*. When the film is developed it is easy to pick out the points at which the density of the second set of bands is equal to that of the first set: that is to say, the points on the time scale (along the length of the film) at which the area of opening of the shutter amounted to 1·0, 0·9, 0·7, 0·5, 0·3 and 0·1 of the full aperture. When these points are being located it is convenient to rest the film on an illuminated opal glass, with a mask which screens off all but the immediate neighbourhood of the point at which the densities match. During the instantaneous exposure a time scale is impressed on the film in the following way. Light from the pointolite ball is reflected by the mirror M_1, figure 1, along a line at a small angle to the axis of the apparatus and crossing the axis at the plane S. The light is made to strike the film at the proper place on the drum by the mirrors M_2 and M_3. This double reflection is necessary to avoid interference by the lenses and mirrors with the light travelling along the axis of the apparatus. The lens L_3 forms an image of the pointolite ball on L_4, and L_4 forms a reduced image of the aperture over L_3 at the central point in the plane S, and this small image is again reproduced

on a still smaller scale on the film by the lens L_5. In this way sufficient light to give a record on the film is transmitted with exceedingly small openings of the shutter. The principle of sending a very small but intense beam of light through the centre of the shutter aperture is that used in the National Physical Laboratory apparatus[2]. Immediately in front of the lens L_3 is mounted a disc with evenly-spaced holes cut near the periphery, and made to revolve at high speed by a small motor synchronized with controlled-frequency alternating current by apparatus of the phonic-wheel type, such as is commonly used in television receivers. The light is interrupted in this way 1995 times a second, which is as near as could be obtained to the desired 2000 times a second, with the a.-c. frequency and apparatus available. For the total duration of opening of the shutter, therefore, flashes of light are being sent through the shutter, and are recorded on the developed film as short, slightly inclined black lines, spaced at intervals along the film corresponding nearly enough to 0·0005 second.

§ 3. UNIFORMITY OF ILLUMINATION OF SHUTTER

It is obvious that for accurate results the intensity of illumination should be uniform over the area of the full aperture of the shutter. Experiment has shown that the pointolite ball is, in itself, satisfactory in this respect. But the condenser lens is not corrected and this causes some difficulty. Chromatic aberration and coma do not cause any serious trouble since the brightness of the image is the same as if there were no such aberration, except for a rim round the edge of the image of the same order of dimensions as the size of the diffuse patch which is formed, in consequence of these aberrations, as the image of a point source. But the spherical aberration is of more consequence: as a result of it, the images given by the different apertures do not overlap exactly. Sufficient overlap exists, however, to give an area 25 mm. in diameter illuminated uniformly by the light from any small element of the condenser. The fact that the brightness of the image produced by each small element of the condenser is not the same as that produced by another element is immaterial, as will be shown later.

§ 4. METHOD OF INTENSITY-COMPARISON

The valuable features of the method using juxtaposed bands of varying density in the photographic comparison of intensities have been pointed out in considerable detail by L. A. Jones[4]. If these features are to be retained properly it is very necessary that the strips be in as exact contact as possible. Therefore the diaphragm and apertures were made very carefully, so that one set of apertures fits precisely in between the other set. Since the areas on the film at which the comparison is made are small and very close together it is not necessary to make special efforts to secure uniform development. For the same reason accurate results are not dependent on the use of sensitive material with more than ordinary uniformity. Again, since the comparison of densities is, in effect, made along the line of contact of two bands, variation in the illumination from different points on the condenser

lens is without effect provided that there is no sudden variation close to the dividing line between two bands or apertures.

The average illumination on the film depends upon the size of the full aperture of the shutter being measured, and in order to keep the density of the record at a convenient level a variable resistance is inserted into the supply feeding the pointolite lamp, so that for large-aperture shutters the intensity of the pointolite ball may be reduced. In this way the same average density may be obtained with a shutter having an aperture 25 mm. in diameter as with one having an aperture 7 mm. in diameter.

At first sight an attempt to obtain bands differing in exposure by reducing the width of the apertures to 0·9, 0·7, 0·5, 0·3 and 0·1 of the maximum is attractive. But it is difficult to do so when, as will be seen later, the maximum width is for good reason only 2 mm. Moreover, apart from this difficulty, the method is theoretically unsound owing to the influence of reciprocity failure.* Reduction of the widths to the above values was in fact found not to give the required reduction in exposure. Even if the aperture-widths were reduced empirically to simulate reduction in intensity to 0·9, 0·7, 0·5, 0·3 and 0·1 of the maximum, there still remained the possibility of the introduction of errors unless the intensity of illumination on the film and the speed of the drum were always the same. The use of neutral filters permits the exposures to be kept of constant duration and thus avoids any difficulties due to reciprocity failure.

Cine positive film is used for the record because it is easy to handle, an orange light being safe enough with it, while its speed is adequate. The contrast is high so that differences in intensity of illumination are reproduced strongly, and determination of the position of equal densities is made easier. Since this material is not colour-sensitized and since much of the ultraviolet radiation from the lamp is lost by absorption in the lenses of the apparatus, the effective sensitivity is restricted to a relatively narrow region of the spectrum, and perfect neutrality of the filters is therefore unnecessary. For the same reason a change in the colour temperature of the pointolite lamp is practically without effect on the effective transmission of the filters. In order to keep the intensity as steady as possible the lamp is run off accumulators: the variation in intensity from one exposure to the next is negligible.

The gramophone motor which drives the drum is driven by controlled alternating current and is found to keep within ± 1 per cent of its average speed. Stroboscopic examination shows that the drum is not subject to sudden fluctuations in speed, such as would average out over a long period and not be detected when the exposure is timed with a stop watch. The position of the drum at any instant during its rotation is shown by an index on the lid of the box enclosing the drum. This index is loosely coupled to the drum (so that the lid may be lifted up for wrapping film round the drum) and rotates in synchronism with it. With the aid of the index

* "Reciprocity failure" is the term used to describe the fact that the density produced under given conditions of development is not a function of the product of intensity of illumination and time of exposure alone, or that, in other words, an x times decrease of intensity is not necessarily compensated for by an x times increase in exposure-time.

t is possible to start and to end the exposure to the apertures fitted with filters at the point on the drum where the film is joined, and also to time the instantaneous exposure of the shutter so that it falls midway between the ends of the film. After practice it is, in fact, quite possible to space out as many as four instantaneous exposures on one film.

§ 5. EFFECT OF FINITE WIDTH OF APERTURES

Suppose that a point x on the film, which is moving with a velocity v, passes under the second edge of the image of the aperture at a time t. If the width of this image is Δ, then the exposure commences Δ/v before t and finishes at t. If the intensity of the illumination passed by the shutter at the time t be represented by $f(t)$, the total exposure at x is $\int_{t-\Delta/v}^{t} f(t)\,dt$. On a band where the illumination is constant and equal to I, the total exposure anywhere along the film is $I.\Delta/v$. The points where the densities of the two bands are equal is given by the value of t at which

$$I.\Delta/v=\int_{t-\Delta/v}^{t} f(t)\,dt$$

or

$$I.\Delta/v=f(t-\tau).\Delta/v,$$

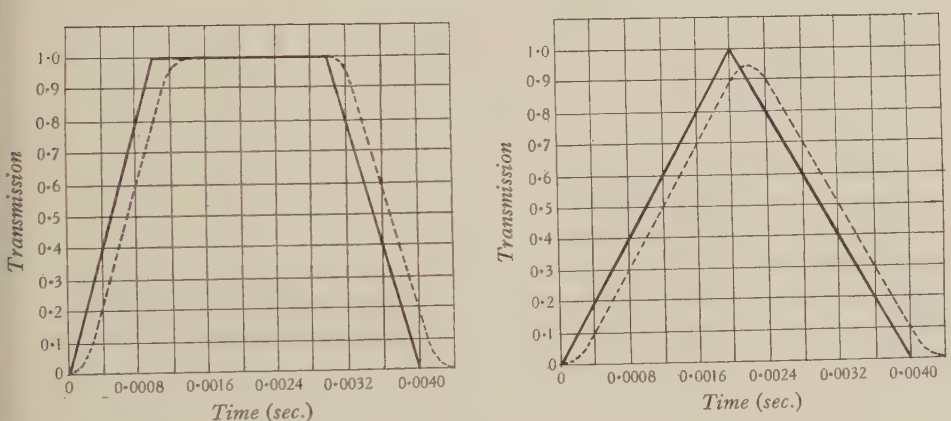

Figure 3. Effect of finite aperture width.

where τ lies between 0 and Δ/v and is such as to make $f(t-\tau)$ equal to the mean value of $f(t)$ over the range $(t-\Delta/v)$ to t. The effect of using apertures of finite width is therefore to displace the curve bodily along the time axis by an amount roughly equal to $\Delta/2v$ where the curve has no sharp curvature over the interval Δ/v, and to round off all sharp bends. The small dot of light which traces out the time scale is therefore made to fall on the vertical centre line of the image of the column of apertures. The amount of distortion of the curve caused by rounding off sharp bends increases relatively at the faster shutter-speeds. However, in the present case Δ is 0·7 mm. and $1/v$ is equal to 0·0006 sec./mm. on the average, so that even at a total time of opening of 0·004 sec. the distortion is not very serious. This is shown by figure 3, where hypothetical curves, as they would be recorded with an

indefinitely small value of Δ (or infinite value of v), are shown by the full lines and the curves as they would be recorded under the conditions stated above are shown by the broken lines.

§ 6. CALIBRATION AND TESTS

The uniformity of illumination over the shutter was tested by exposing process film* placed at the plane S, only one of the apertures being used over the condenser lens. The density-distribution over the resulting image was measured after careful development and fixation, and it was found that over an area 25 mm. in diameter there was no variation in intensity greater than ± 5 per cent, whichever aperture was used. A variation of this amount is practically negligible for the present purpose. Indirect proof of the uniformity of illumination is also provided by the tests on shutters for which the curves relating time with area are known.

As the filters had not the same transmission at all wave-lengths, it was necessary to reduce them to the correct thickness empirically. This was done with the apparatus in the following way, and it may be noted that if any variation of intensity were centrally symmetrical, as variations are of course most likely to be, the method of calibration would tend to reduce its effect on the final result when shutters are being tested. A set of circular apertures was made to fit into the shutter-holder, the largest being 20 mm. in diameter and the remainder having areas 0·9, 0·7, 0·5, 0·3 and 0·1 times that of the largest. Exposures were made through them in succession to successive apertures of the set without filters, figure 1 B. The second set of apertures was then rotated into position and covered with a piece of the neutral glass in its original thickness, and an exposure was made to these apertures through the 20-mm. circular aperture. By measurement of the densities of the various bands, the glass was found to have an effective transmission of a little under 10 per cent. From this figure estimates were made of the thicknesses giving the required transmissions, and pieces of the glass, ground and polished to these thicknesses, were placed in the appropriate apertures. For the 0·9-transmission aperture a piece of plate glass was used, as it was expected that the combined absorption and reflection losses due to this glass would reduce the transmission very nearly to the value in question. The previously described operations of exposure through the apertures in the shutter-holder were again carried out. When the densities of the bands on the developed film had been measured, the densities of the bands exposed through the set of shutter apertures were plotted against the relative areas of the shutter apertures. The transmissions of the filters were then read off this curve from the value of the densities of the bands exposed through the filters and the 20-mm. shutter aperture. This is allowable if the filters are in their final order on the diaphragm and if the exposures through the shutter apertures are made so that bands of the same nominal intensity (one through the filter and one through the corresponding shutter aperture) are adjacent. For then by measuring the densities over small areas (1 mm. in diameter) close to the line

* Process film was used since it will, by its high contrast, exaggerate any non-uniformity of illumination.

dividing the strips, the effect of different light transmission through different parts of the condenser is almost eliminated. A nearer approximation to the required thickness is thus obtained. It has also been found in this way that alteration of the intensity of the pointolite lamp (by lowering of its temperature) is without measurable influence on the effective transmission of the filters.

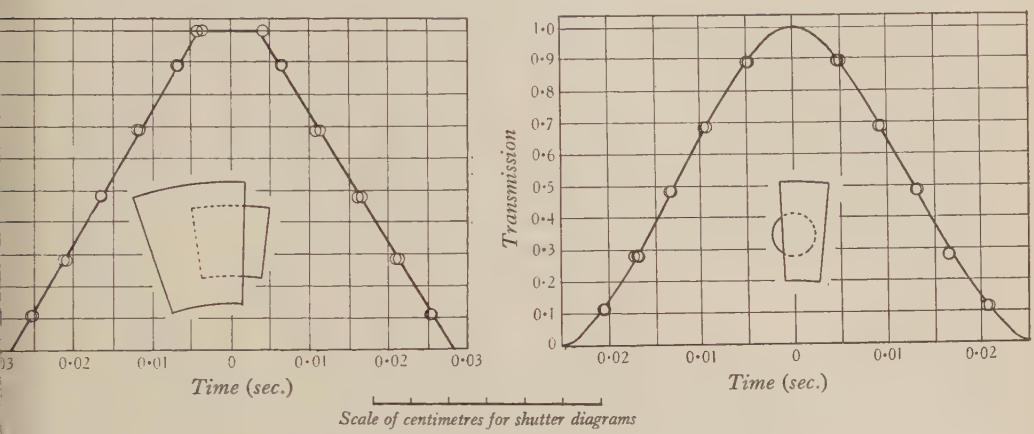

Figure 4. Experiments on shutters with known efficiency curves.

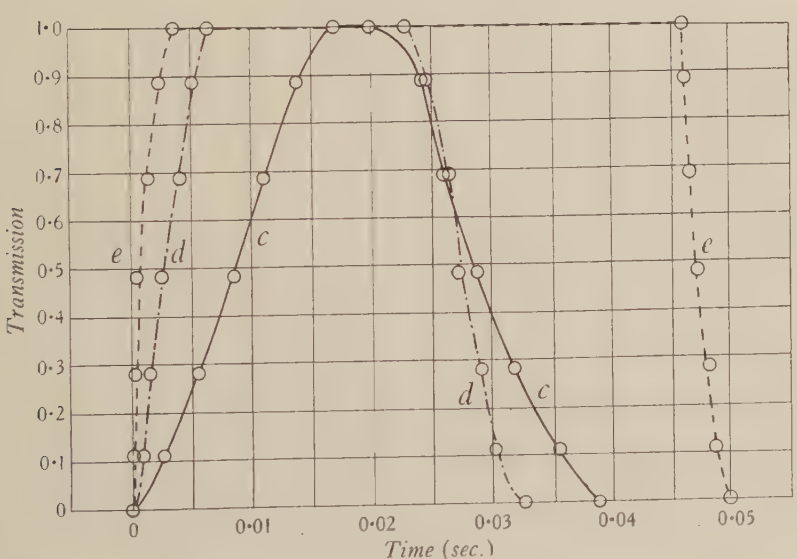

Figure 5. Three commercial shutters.

The transmissions of the filters as finally used were measured in the above way and found to be

0·11, 0·28, 0·48$_5$, 0·69, 0·89.

It is regarded as very unlikely that any of these values is in error by more than ±0·01.

Tests have been carried out on two shutters for which the curves relating area with time could be calculated. These consisted of sector apertures rotated at constant speed by a synchronous motor over either a sector-shaped or a circular fixed aperture. The shapes and sizes of the shutters are indicated in figure 4, together with the calculated curves relating area with time and the observed points. Two experiments were made on the first shutter and three on the second, and all observations are plotted. From these tests it appears to be unlikely that an experimental error greater than 0·02 in the transmission would be found anywhere on the curve.

In figure 2 at *c*, *d* and *e* are shown the records obtained from three different commercial shutters all set to a nominal $\frac{1}{25}$ sec., and in figure 5 the efficiency curves derived from the records in the ordinary way.

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TIME AND AMPLITUDE RELATIONS IN SEISMOLOGY

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ABSTRACT. The paper deals with certain anomalies in the amplitudes of the waves observed in near earthquakes, and their relation to the method of transmission across interfaces. It is suggested that amplitude-observations in seismic prospecting may help to solve these theoretical problems. A rediscussion of the time relations shows that these are so closely related to the structure immediately below the observing station that the form of the interfaces produces no other appreciable effect.

Some years ago I published a paper[1] on compressional waves in two superposed layers, which appears to have attracted an amount of attention in seismic prospecting that I should never have anticipated. The work described in it was done with the object of finding out whether the possibility of diffraction along an interface would explain the observed variation with distance of amplitude of vibration in near earthquakes. It failed in its purpose in two respects, and I am not yet able to ascertain from the literature whether it succeeds any better in its application to seismic prospecting. Without wishing to appear ungracious, I think that it is desirable to call attention to the outstanding difficulties.

The elementary theory of elastic waves from a local source shows that the amplitude should vary inversely as the distance.* In near earthquakes—those well observed at distances less than a few hundred kilometres—the observed amplitudes diminish with distance, but definitely less rapidly than the inverse square of the distance; the actual variation is irregular, but roughly as the inverse distance.† This would be satisfactory if it were not for two complications. The motion of the ground depends not only on the incident waves, but also on the reflected ones, and for a *P* wave at grazing incidence the effects of these two just cancel.‡ To explain the existence of any ground-motion it seems necessary to take the depth of the focus into consideration; but when we do this and allow for the conditions of reflection we find that a factor depending on the angle of emergence enters, and the result is that the ground movement should vary as the inverse square of the distance.§ This applies to direct waves. For waves that have travelled in a lower layer the angle of emergence is always finite, and this complication does not arise. But when the path in the lower layer is nearly horizontal the loss of energy by reflection in crossing the interfaces is very great. If we adopt the usual theory and suppose the energy to travel along the rays, correcting for this loss, we find

* See reference (2), p. 282.
‡ See reference (4), p. 327.
† See reference (3), p. 400.
§ See reference (4), p. 336.

that the variation of amplitude with distance disappears at short distances; the greater amplitude in the original wave is cancelled by the greater loss on reflection when the path in the lower layer is nearly flat.* This conclusion again disagrees with the facts, the observed amplitudes being again roughly as the inverse distance.

My paper was intended to find out whether these results would be altered if we allow for diffraction at the interface and ignore the curvatures of the rays and the interface, the difference of which is what matters in the elementary theory. For its original purpose the work was a failure. The surface motion due to the direct wave was still as the inverse square of the distance. There was an indirect wave, which would not exist at all in these conditions on the ordinary theory, but it still disagreed with observation. If the direct wave begins with a finite velocity, the indirect one should begin with a finite acceleration; the shorter periods present in the direct wave should therefore be smoothed out in the indirect one. The acceleration also should vary as the inverse square of the distance. Actually the indirect wave, except for being smaller, is very like the direct one; and short periods are equally prominent.

It seems to me that the amplitude relations are capable of only one interpretation, namely that the angle of emergence of the direct waves is always finite and much the same at all distances, and that the same applies to the angle of emergence of the indirect wave at the interface. In this way the troublesome extra factors are avoided. But this cannot be achieved in accordance with the ordinary law of refraction. We seem to need scattering, such as occurs in the case of light at the surface of ground glass. In near earthquakes this may be due to minor irregularities in structure, and possibly in the form of the interface. How far this applies to the conditions of seismic prospecting I am not in a position to say, but I think that this field of study may give valuable information, since the form of the interface is there ascertainable. For comparison with the results of the study of near earthquakes I should like to know how the amplitudes do in fact vary with distance, whether there is any systematic difference between the direct and indirect waves in respect of the prominence of short periods and sharp onsets, and how these relations vary according as the interface is plane, anticlinal or, if possible, synclinal. In these respects seismic prospecting may make a valuable contribution to pure seismology.

The various theories all give the same results for the times of arrival of the pulses. A little more discussion of the effect that arises when the interface is not horizontal, however, seems to be desirable. In works dealing with seismic prospecting a formally exact formula, which is correct for a plane sloping interface, is usually given. But the time is obviously unaffected by the slope of the interface at any point other than those of entry into the lower medium and emergence from it, and if the interface is anticlinal the mean slope will in general differ from the actual slope at both these points. The exactness of the formula is therefore only apparent. There may be advantages in replacing it by an adaptation of the corresponding formula

T used in the study of near earthquakes. The time T of transit is $\int ds\, c$, taken along the

s, c, v path, where ds is the element of length and c the local velocity. If v is the velocity

x, e at the lowest point of the path, x the horizontal distance reached, and e the angle

* See reference (4), p. 340.

f emergence at any point (that is, the angle between the ray and the horizon), we an write this

$$T=\frac{x}{v}+\int\left(\frac{\sec e}{c}-\frac{1}{v}\right)dx \qquad \ldots\ldots(1).$$

ut if z is the depth, $dz=\tan e\,dx$, and

$$T=\frac{x}{v}+\int\left(\frac{\sec e}{c}-\frac{1}{v}\right)\cot e\,dz \qquad \ldots\ldots(2).$$

Where the stratification is horizontal we have, by the law of refraction,

$$\cos e=c/v \qquad \ldots\ldots(3),$$

$$T=\frac{x}{v}+\frac{1}{v}\int\left(\frac{v^2}{c^2}-1\right)\left(\frac{v^2}{c^2}-1\right)^{-\frac{1}{2}}dz$$

$$=\frac{x}{v}+\int\left(\frac{1}{c^2}-\frac{1}{v^2}\right)^{\frac{1}{2}}dz \qquad \ldots\ldots(4),$$

he root being taken positive on the downward path and negative on the upward path[5]. The coefficient of dz in the integral has been called the "delay depth coefficient" by A. W. Lee[6]. For a single upper layer of depth H, with a surface focus, we have

$$T=\frac{x}{v}+2H\left(\frac{1}{c^2}-\frac{1}{v^2}\right)^{\frac{1}{2}} \qquad \ldots\ldots(5).$$

For a sloping interface equation (2) is still exact but (3) is altered, e being changed by a small quantity of the order of the slope of the interface. But it is easy to see that the effect on (4) is negligible. We are still at liberty to consider a ray whose inclination in the upper layers is determined at every point by (3). In the lower layer we must consider it as straight but inclined to the horizon at a small angle α. For this part of the path

$$\frac{\sec e}{c}-\frac{1}{v}=\frac{1}{v}(\sec\alpha-1) \qquad \ldots\ldots(6),$$

and is small, of order α^2/v. Hence to the first order in α the time of the ray is still given by (4), where the integral is taken through the upper layers with their actual thicknesses at the places of entry and emergence.

Such a ray does not strictly satisfy the laws of refraction, because e is altered by quantities of the order of the slope of the interface at the points of entry and emergence. But the time of transit is stationary for small variations of the path, and therefore (4) differs from the true minimum time by small quantities of the order of the squares of the slopes. Thus, finally, if we write

$$T=\frac{x}{v}+\int\left(\frac{1}{c^2}-\frac{1}{v^2}\right)^{\frac{1}{2}}|\,dz\,| \qquad \ldots\ldots(7),$$

where the integral is taken through the upper layers and the root is always taken positive, the error committed is of the order of the squares of the slopes, and in practical conditions is negligible. When the result is stated in this form we see that the

delay in transmission due to the overburden depends on the velocities and on the depth of the overburden near the ends of the path, and only to an unimportant extent on anything else.*

a As an example, let us consider explosions at two points O and A at a distance a, and suppose that there is a third point of observation P on the line joining them
$, H_2, H_3$ and distant x from O. The depths at O, A and P are H_1, H_2, H_3. Denote the delay-
η depth coefficient by η. Then

$$T_{OA}=T_{AO}=\frac{a}{v}+\eta\,(H_1+H_2),$$

$$T_{OP}=\frac{x}{v}+\eta\,(H_1+H_3),$$

$$T_{AP}=\frac{a-x}{v}+\eta\,(H_2+H_3).$$

Hence
$$T_{OP}+T_{AP}-T_{OA}=2\eta H_3,$$

so that H_3, which is what we wish to know, is directly determined. This of course assumes that the velocities are known already. But if we have a further observation
y, H_4 point Q distant y from O, where the depth is H_4, we obtain

$$T_{OP}-T_{OQ}=\frac{x-y}{v}+\eta\,(H_3-H_4),$$

$$T_{AQ}-T_{AP}=\frac{x-y}{v}-\eta\,(H_3-H_4),$$

whence v is determined by addition. The velocity in the overburden needs to be determined independently.

This argument naturally adds nothing to the present technique, but it shows that the usual methods are more directly related to the depth to be found than might be supposed from the form in which the subject is usually presented.

* I gather from a referee's remarks that a similar point has recently been made by Dr J. H. Jones, but I have not yet seen his paper [7].

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DISCUSSION

Prof. A. O. Rankine. I am glad that the author has given the Society this rediscussion of the basis of the so-called refraction method in seismic prospecting. It is true that recently this method has largely given place to the reflection method, but it retains its importance as giving more information about the nature of underground strata. The author's present contribution will tend to prevent waste of time in seeking formally exact solutions in structural problems which do not really justify the attempt. In particular it provides a means of mapping underground contours of small relief over large areas. As the author mentions, Dr J. H. Jones has at least partially recognized the closeness of the relation between local depth and time of propagation of the indirect disturbance, and has used it to map limestone contours in Persia.

With regard to the author's query as to whether the seismograms obtained in seismic prospecting may serve to elucidate the mechanism of the production of the indirect disturbance, I should say probably not, with the possible exception of those obtained with J. H. Jones's seismometer. The majority of portable seismometers, having been designed primarily to detect the time of the first onset of the disturbance whether direct or indirect, are by no means free from resonance, and the form of the record is not a true representation of the earth's movement. I suggest that the author should, if possible, examine some of the many seismograms Dr Jones has obtained from the point of view mentioned above. I hope that he will eventually be able to give us the true explanation of the phenomena, which are real enough.

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ADSORPTION OF GASES ON MERCURY

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ABSTRACT. A mercury surface was formed in the presence of a gas and the gas was pumped off after an interval. The mercury surface was then caused to collapse. This caused an evolution of gas which was measured with a McLeod gauge. For air, hydrogen and carbon dioxide the limiting amount evolved corresponded to a monomolecular layer. This layer appeared to be retained by the surface for a long period. If adsorption beyond a monomolecular layer occurred the subsequent layers were desorbed on evacuation.

§ 1. INTRODUCTION

Some years ago Prof. Kerr Grant suggested to the author the problem of investigating the spreading of liquids, particularly water and aqueous solutions, on the surface of mercury. The discussion of the phenomena observed demands a knowledge of the surface tension of mercury both in air and against its own vapour, as well as of the interfacial tension between mercury and the liquids used. Reference has been made elsewhere to the extreme confusion in the literature regarding both the value of the surface tension of mercury and the action of gases on its surface, and several papers from this laboratory have described work carried out on these subjects[1-8].

Briefly the position was that workers using the method of the sessile drop obtained values of about 440 dyne cm. for the surface tension of mercury against its own vapour, but for surfaces formed in gases the initial values were about 500 dyne/cm., falling rapidly at first and then more slowly to the value for vacuum or lower. These results were accepted by authors of standard text books. Now the drop-weight method is almost the only other one than can be applied to determine surface tension both in gases and in a vacuum, and experiments made here[2] as well as the very careful work of Harkins[9] showed that this method yielded very nearly the same value for the surface tension in air as in a vacuum. There was thus the problem of the actual value of the surface tension of mercury and also of the behaviour of its surface with respect to gases. By means of an apparatus constructed of fused silica and the method of the sessile drop the surface tension was determined in a high vacuum and also in the presence of air, both dry and moist[8]. This yielded essentially the same value for the surface tension in gas and in a vacuum (as was indicated by drop-weight measurements), and showed that differences between these values observed by various workers could not be attributed merely to the presence or absence of the gas.

The question whether gases were really adsorbed by the mercury was attacked by Oliphant[5] who found that drops of mercury formed in an atmosphere of either argon or hydrogen containing as much as 2 per cent of carbon dioxide became almost completely covered with a layer of molecules of carbon dioxide by the time the drops had fallen 1 ft. through the mixture (i.e. within $\frac{1}{4}$ sec. after formation). Bosworth[7] confirmed this result and extended the measurements to sulphur dioxide and to water vapour. These apparently represent the first direct measurements of the amounts of gas adsorbed at a mercury surface, though Iredale[10] had estimated the adsorption of vapours by applying the Gibbs adsorption equation to measurements of surface tension, and Sissingh and Haak[11] and more recently Herschkowitch[12] have estimated the condensation of gases on the surface from variations in the optical properties of the surface when exposed to the gas. The theory of this last method has been discussed by Tronstad and Feachem[18, 19].

Oliphant's results for carbon dioxide in hydrogen leave three possibilities as to the behaviour of these gases and hydrogen: (i) that carbon dioxide but not hydrogen is adsorbed by the expanding mercury surface; (ii) that hydrogen is adsorbed but that its life on the surface is extremely short compared to that of carbon dioxide; (iii) that hydrogen by itself may be adsorbed and persist on the surface but that the presence of the carbon dioxide actually causes the hydrogen to be desorbed.

Either the first or the second of these assumptions gives a simple picture of the process occurring at the surface but neither of them can be reconciled with the results of the present work or with sundry observations recorded in the literature[13, 14] regarding the reaction of hydrogen and mercury. Bosworth's results indicate that when carbon dioxide and water vapour are each present, the relative amounts present in the adsorbed layer and in the gas are not the same, as would be the case if each kind of molecule were adsorbed on impact and had a considerable life on the mercury surface independently of the other active substance*.

The aim of the present work was to determine whether gas adsorbed on the surface of mercury leaves the surface as the gas pressure above it is reduced to low values, and if it does not, to measure directly the amounts adsorbed by both static and expanding surfaces. Calculation shows that a monomolecular layer of gas over a surface of moderate area involves a quantity of gas sufficient to give a measurable pressure in an apparatus having a volume of a litre or more. Owing to the vapour pressure of the mercury itself it was impossible to use any of the special types of manometer such as ionization or Pirani gauges, and a McLeod gauge giving a reading of 2·3 cm. for a pressure of 0·001 mm. was used.

The original idea was to form a surface some 400 cm^2 in area in a flat chamber in the presence of the gas, to exhaust to a low pressure, and then to measure the gas evolved when the surface was destroyed by allowing the mercury to flow out through a narrow tube at the bottom. It was necessary to be able to form the surface

* Bosworth's results are of course also explicable if we assume that only a fraction of the molecules striking the surface are adsorbed and that this fraction is different for different gases, but the available evidence does not appear to contradict the view that practically all the molecules which strike a metal surface condense thereon.

and to run the mercury out with the apparatus exhausted without the use of any taps, lubricated or otherwise, since lubricants would contaminate the surface and unlubricated taps either seize or else slip out under the weight of a large head of mercury.

The flat chamber was prepared by grinding a circular depression in a slab of $\frac{3}{4}$-in. plate glass and covering it with a similar slab, the two being sealed together by a special optical cement. After much trouble it was found that even such thick glass always yielded sufficiently under atmospheric pressure to crack the seals. Though leak could be prevented by an outer plastic coating round the seal there remained the probability of gas being entrapped in cracks in the seal and slowly escaping to vitiate the measurements, especially as the whole quantity of gas expected in the apparatus would be less than 0·001 c.c. at atmospheric pressure. Accordingly the flat chamber was replaced by a vessel made from a tube of pyrex glass of large size and the apparatus redesigned and constructed wholly of pyrex glass sealed into one piece. The new chamber only permitted a much smaller surface being formed (60 sq. cm.), but a monomolecular layer over this area would yield gas sufficient to give a pressure of about 0·0012 mm. in the apparatus and this could easily be measured with the required accuracy. Moreover the new apparatus could be strongly heated, thus making it much easier to remove water from the glass walls and so bring them to a steady state in regard to adsorption and emission of gases.

§ 2. APPARATUS AND METHOD

The vessel *B*, figure 1, was made from pyrex tubing 7 cm. in bore. It was fixed almost horizontally as shown, so that mercury from *A* could be allowed to flow into it, forming a surface of area 60 cm^2. The mercury reservoir *A* was situated about 3 ft. from *B* and connected thereto by glass tubes *C* and *D* about 2 mm. in bore. These were sufficiently flexible to permit *A* to be raised or lowered through a distance of 6 or 7 cm. The tube *D* allowed the gas in *A* to adjust itself to the same value as in the rest of the apparatus. The reservoir *A* was carried on the slide-rest of a lathe. This was firmly bolted to the bench in a vertical position, enabling *A* to be raised or lowered fairly quickly and without risk of exceeding the limit of flexibility of *C* and *D* or of imposing irregular strains on them. Thus the mercury could be caused to flow into or out of *B* without the use of taps or valves and independently of the gas pressure in the apparatus.

B was sealed directly to the Langmuir pump and McLeod gauge by wide tubing to allow rapid pumping and equalization of pressure in the apparatus. The pumps were not mounted on the same bench as the apparatus, so that their operation would entail a minimum of vibration of the mercury surface in *B*.

The narrow tubes *E* and *F*, open at the lower ends, dipped into vessels of mercury so that when the apparatus was exhausted the mercury stood just below the join as at *K*. Hence when the vessels *G* and *H* were raised, the chamber *B* and the gauge were isolated from the rest of the apparatus by mercury cut-offs, so that any gas evolved from the mercury could produce a maximum increase in pressure and

be measured more rapidly. Even if a leak were to occur at the gas-inlet M or the mercury seal L it would not affect the reading when G and H had been raised. To attain rapid pumping it was necessary to avoid having to evacuate A through the long narrow tube D and this was done by raising H a few seconds after starting the pump, when the pressure would have fallen to a fraction of a millimetre.

During the construction of the apparatus the glass tubing was carefully cleaned, and the separate parts were again cleaned before being sealed together in situ. The whole was then steamed out and dried with an air current before being sealed to the pump. To remove occluded moisture from the walls the apparatus was heated for some time while subject to high vacuum. For this purpose B was surrounded by a woven electrical resistance and the narrow tubes were wound with thin wire and heated electrically. The wide tubes could be safely heated with a flame. The mercury was cleaned by distillation under reduced pressure in a slow air current and by washing, as described elsewhere[1,8].

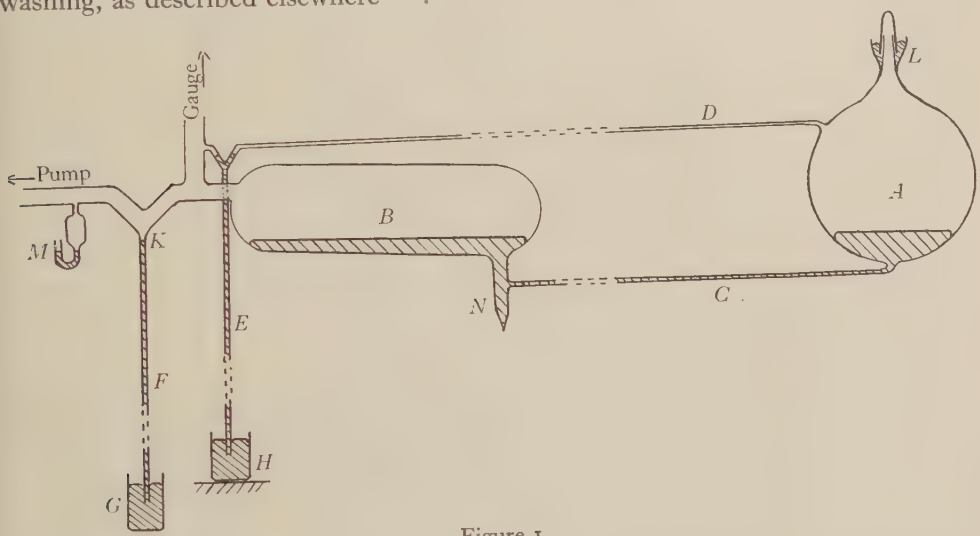

Figure 1.

To place the mercury in the apparatus, A was lowered as far as possible, some mercury was poured in, and the seal L was closed. The apparatus was then exhausted and the tube was made hot by means of its winding of wire, after which A was slowly raised. This avoided the possibility of any gas being trapped in C or N, the mercury being actually boiled in each of these. The mercury could be removed for re-distilling by snipping off the tip of N.

An experiment consisted essentially of the following operations: (*a*) gas was admitted up to the required pressure through inlet M; (*b*) A was raised and a mercury surface of area 60 cm^2 was thus formed in B; (*c*) after an interval the gas was pumped out, E and F were closed as has been explained, and the pressure was measured; (*d*) A was lowered causing the surface to collapse, the mercury flowing out till it stood at the top of the tube N; (*e*) the pressure of gas in the apparatus was measured.

§ 3. EFFECT OF ADSORPTION BY WALLS OF APPARATUS

In most previous work on the direct measurement of adsorption, the gas has been admitted at a low pressure only and the reduction of this pressure was noted as adsorption proceeded. The walls were not subjected to large changes of pressure and the area of adsorbing surface (e.g. in charcoal) was large compared with the walls, though this area was not usually directly measurable.

In the present experiment the mercury surface represents only a few per cent of the area of the inside of the apparatus. Moreover the walls are alternately subjected to atmospheric pressure of gases and then a pressure of 10^{-4} mm. Hence it was necessary to consider the possibility that adsorption and desorption of the glass might complicate or perhaps obscure the effects due to the mercury. Tests were made, without mercury in B, of the rate at which gas was evolved from the walls after these had been exposed to gas at varying pressures and for varying periods. These tests showed that once the glass had been thoroughly dried by prolonged heating in a high vacuum it became consistent in behaviour. Since the experiments involved the use of only dry gas, and since the apparatus did not vary appreciably in temperature, the simple procedure outlined below enabled the gas evolved from the mercury to be measured with sufficient accuracy. Observations were also made of the effects of raising the temperature of the apparatus through 100° C., and it was found that though consistent results were obtained the amount of gas evolved was sufficiently large to make it difficult to disentangle the effects due to the mercury from those due to the walls. An interval of 5 min. was found sufficient for the pumps to give the necessary stage of exhaustion, and this period also allowed the mercury to flow either into or out from B and become stationary.

In making an observation gas was admitted to the required pressure and A was then raised, causing the mercury to flow into B, where it was allowed to stand for periods varying from a few minutes (the time for the mercury to come to rest) up to several hours. The condensation pump being already hot, the backing pump was started and the cut-off at E was raised after a few seconds and that at F after 5 min. The pressure was then read on the gauge and the reading was repeated, usually at 5-min. intervals. During one of these intervals A was lowered, destroying the mercury surface in B. The graph of pressure against time shows by a sudden rise in this interval the effect of the gas liberated from the mercury, and this can be quite well separated from the slow evolution of gas from the walls, even though this factor varied considerably with the pressure of gas and the time it had been retained in the apparatus. By variation of the period between exhaustion and collapsing of the surface it was shown that the adsorbed gas was retained by the mercury for a considerable time.

§ 4. ADSORPTION AND LIFE OF CARBON DIOXIDE ON THE SURFACE OF MERCURY

The gas was admitted from a high-pressure cylinder through a series of drying tubes and filters of glass wool. A thin rubber diaphragm over a side tube acted as a safety valve to protect the apparatus against high pressures.

A pressure of 10^{-4} mm. would correspond to a total of 29×10^{14} molecules at laboratory temperature in the whole volume of B, the gauge, and the wide connecting tube. A monomolecular layer of gas over the 60 cm^2 of mercury would, on complete desorption, yield approximately 34×10^{15} molecules and thus cause a rise in pressure of 12×10^{-4} mm.

In figure 2 a typical selection of curves is given showing the rise in pressure which occurred on collapse of the surface, the time in each case being measured from the instant when the cut-off F was raised. Other details of the experiments are

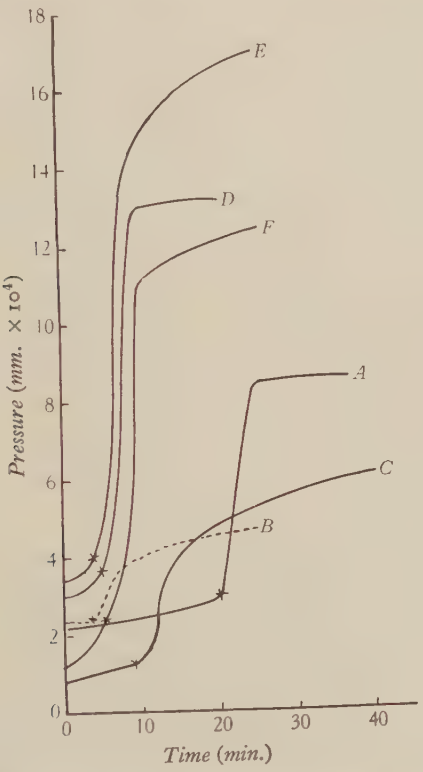

Figure 2. × indicates point at which surface was collapsed. A: CO_2, $p = 10$ cm., exposure 2 h. B: Hg admitted first, then 12 cm. of CO_2. C: CO_2, $p = 8$ cm., exposure 48 h. D: CO_2, $p = 36$ cm., exposure 20 min. E: CO_2, $p = 76$ cm., exposure $2\frac{1}{2}$ h. F: CO_2, $p = 76$ cm., exposure less than 10 min.

given below the figure. The curve B indicates the small amount of adsorption detected when the mercury surface was formed in a fairly high vacuum and the carbon dioxide subsequently admitted. A comparison of the curves shows how much less readily adsorption occurs under such conditions than in the case when the surface is formed in the presence of the gas. This fact is in keeping with comments by writers on the differences observed between a static mercury surface and one that is expanding or freshly formed. The observed rise in pressure due to liberation of carbon dioxide varied from about 4×10^{-4} mm., when the surface had been formed

in carbon dioxide at a pressure of 8 cm., to almost 12×10^{-4} mm. when the surface had been formed in the same gas at atmospheric pressure. The latter amount corresponds to practically a complete monomolecular layer. The time of exposure, as was expected, had little effect on the amount of gas retained by the surface. It is just possible that very long exposure resulted in less gas being recovered (as in *C*) owing perhaps to something replacing the carbon dioxide on the surface. The observed variation of the amount adsorbed with the pressure of gas is hardly to be expected, however, if the adsorbed layer of gas is retained by the surface: see § 6. On a number of occasions the mercury surface was formed in gases at pressures of about 0·001 mm., but in no case did measurable adsorption occur at this pressure under the experimental conditions pertaining.

§ 5. MEASUREMENTS ON HYDROGEN AND DRY AIR

Experiments were also carried out with hydrogen, which was passed through a tube containing heated platinized asbestos before reaching the drying train. Measurements showed the same general features as in the case of carbon dioxide, the gas being retained by the surface on evacuation as was indicated by the observations of Cook [13]

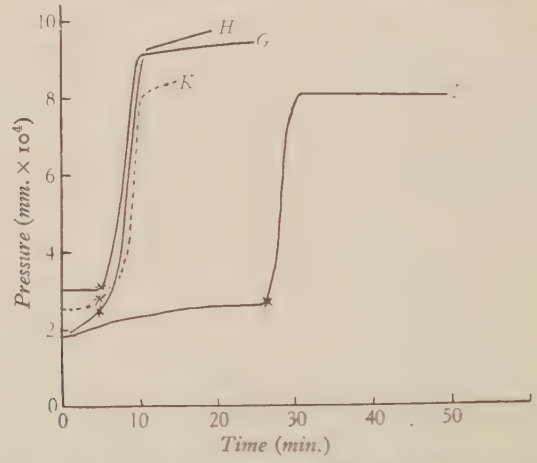

Figure 3. *G*: H_2, $p = 40$ cm., exposure 35 min. *H*: H_2, $p = 40$ cm., exposure 35 min. *K*: Air, $p = 45$ cm., exposure 5 min. *L*: CO_2, $p = 50$ cm., exposure 10 min.

though there was some suggestion that the mercury surface would lose some of the adsorbed hydrogen more easily than it lost carbon dioxide. Curves *G* and *H*, figure 3, are for readings made some months apart. The curve *K* is for air admitted through the drying tubes and indicates an adsorption of the same order as for hydrogen, though it is of course possible that the adsorbed gas did not have the same proportions of oxygen and nitrogen as the air. Curve *L* is for carbon dioxide when a period of nearly half an hour elapsed between the evacuation and collapse of the surface. The flatness of the curve both before and after collapse of the surface indicates that the adsorbed layer was not being lost at an appreciable rate in a vacuum of 2×10^{-4} mm., and also shows that very little gas was evolved from the glass, at any rate after the first 5 min.

Tests were made at times of the effect of bumping the apparatus before collapsing the surface and it was found that the surface could be caused to oscillate a good deal without any appreciable evolution of gas.

§ 6. DISCUSSION OF RESULTS

When a mercury surface is formed in any of the gases carbon dioxide, hydrogen, or air an adsorption occurs at the surface, the limit apparently being a monomolecular layer, which in these experiments was only approached as the gas approached atmospheric pressure. Little, if any, other work has been published with reference to direct measurements of adsorption of gases on mercury. Both Oliphant and Bosworth measured the amount of gas adsorbed selectively from mixtures at atmospheric pressure, and by using a shower of drops ensured that they were always dealing with a freshly formed surface. This is an important consideration since even under the very best experimental conditions the properties (e.g. the surface tension and the photo-electric effect[20]) of a mercury surface at rest are seldom found to agree with those of an expanding surface.

Sissingh and Haak[11] in 1919 observed the change in optical properties of mercury with time of exposure to air and estimated that the thickness of the adsorbed layer was about $1{\cdot}6\mu\mu$. More recently E. Herschkowitch[12], working on the same subject, has reported that neon and nitrogen produce no measurable effect but that hydrogen, oxygen, and carbon dioxide appear to be absorbed in layers varying in thickness from 5 to 15 molecular diameters. The present work makes it clear that if such thick layers do condense on the surface then all layers beyond the first must be so loosely bound as to be at once desorbed on evacuation, whereas the first layer appears to have an almost indefinite life on the surface. Herschkowitch[12] does in fact record a partial recovery of the mercury surface when the space above it is evacuated, which suggests that part of the observed optical effect is due to an adsorption which is reversed on evacuation.

Stoeckle[14] records an evolution of gas from a mercury surface and Cook[13] records the following observations in his paper on the surface tension of mercury: "In one case the tension of mercury in contact with hydrogen at 0·00015 mm. remained constant at 421 dynes over a period of 8 min. On spilling a drop from the mercury (thus breaking the surface) the tension immediately rose to 463 dynes and remained at this value for 14 min. Simultaneously the pressure of hydrogen rose to 0·00048 mm.;" and later "the tension in hydrogen decreased from 475 dynes to 484 dynes in 20 min. while the pressure fell from 0·0037 mm. to 0·0020 mm." The significance of the periods of time stated is not clear, but it does appear that under the conditions which must be attained for accurate surface tension measurements the mercury adsorbs hydrogen at quite low pressures. The figures given by Cook show that an evolution of gas sufficient to raise the pressure by 0·00033 mm. was accompanied by a rise of 52 dyne/cm. in surface tension, yet a fall of only 11 dyne/cm. was accompanied by a fall in pressure 0·00170 mm. If these figures could be taken as due to effects occurring at the mercury surface only, it would mean that the

adsorption per fall of 1 dyne/cm. in surface tension was more than 25 times as great as the amount desorbed for an equal rise in surface tension. In the absence of any other information about the actual conditions obtaining, it seems most probable that all the gas evolved came from the mercury but that the glass walls were contributing to the observed adsorption, since it is unlikely that actual solution of the gas in the mercury could account for more than a fraction of the difference.

The significance of the variations of the amount of gas evolved from the surface with the pressure of gas to which the surface was exposed is by no means clear. Since the adsorbed molecules have a long life on the surface, it is to be expected that a complete monomolecular layer would be adsorbed and retained from gas at a pressure of 8 cm. equally as well as from gas at atmospheric pressure. There is, however, a striking parallelism between these results and those obtained for the surface tension by some of the workers using the method of the sessile drop. Thus Popesco[15] found the initial value of surface tension highest for a surface formed in gas at atmospheric pressure, with lower values when the surface was formed in gas at lower pressures, the lowest value being for the surface formed in a vacuum; but that the subsequent admission of gas to the surface did not cause any rise in the surface tension. Consistently with this the author finds that very slight adsorption occurs when the surface is formed in a vacuum and the gas admitted later, and that for a surface formed in the gas the adsorption is larger for higher pressures.

Explanations of the above-mentioned variations of surface tension have been advanced in terms of the orientation of the molecules to positions of minimum energy. These explanations are open to objection and it is in fact now found that the surface tension of mercury is not lower in a vacuum than in gases. In spite of the work of Hiss and others, N. K. Adam[16] concludes that there is no satisfactory evidence that the surface tension of any pure liquid changes with time. The low values of surface tension of mercury must be ascribed to some factor acting as a contamination, though it has never been possible to establish the nature of this contamination. In the present work, owing to the effect of the glass it was useless to proceed to the very high vacuum obtained by prolonged degassing, and it is probable that the same influences which caused the lower surface tensions at reduced pressures were present here, this contamination occupying some of the surface and preventing adsorption at very low pressures. Cook, was able, however, to detect the adsorption when working under the conditions necessary for surface-tension determinations. The present work shows that it is possible to measure adsorption on mercury by a direct method. The advantage of having a perfectly definite area of surface (as contrasted with the surface-area of charcoal, powders, or crystalline aggregates) is largely offset by the uncertainty which still exists as to the actual cause of the variations to which reference has just been made. Evidence indicates, however, that adsorption approximately to the extent of a complete monomolecular layer occurs on mercury surfaces formed in gases at moderate pressures, the adsorption probably being complete by the time the surface has come to rest. This layer persists on evacuation in spite of considerable oscillation of the surface, but is liberated when the surface is destroyed.

Freundlich accepts the view that the fall in surface tension in gases is due to adsorption, and says that no fall of value with time occurs in a vacuum, as is to be expected with an unassociated liquid. No suggestion is offered as to the cause of the higher initial values for gases which are quoted. Freundlich further states that the adsorption is very rapid, "the process requiring a finite time being a diffusion in a very thin layer." A critical survey of all the available data on the effect of gases on the surface tension on mercury shows that agreement between workers is far from satisfactory. There seems no doubt that a monomolecular layer is adsorbed practically before any appreciable fall in surface tension has occurred. If this single layer is the cause of the fall in surface tension observed by various workers over periods of hours or days, the adsorption and surface tension can scarcely be connected by an equation such as that of Gibbs.

On the other hand if the subsequent fall in surface tension is due to the adsorption of polymolecular layers (the existence of which is suggested by Herschkowitch and others) it is not to be expected that these layers should be desorbed so readily in comparison with the initial layer. It is of course possible for a large reduction of surface tension to be caused by a layer that is lost on evacuation. Some unpublished observations by Prof. Kerr Grant show that the surface tension of water falls by over 20 per cent. in the presence of ether vapour, but recovers almost completely as soon as the ether vapour is allowed to escape. Moreover S. G. Cook does record a considerable recovery in the surface tension of mercury which has been exposed to air or oxygen if the pressure of the gas is lowered, though it never rises to the initial value for a vacuum. The mercury requires a long time to reach equilibrium with a given pressure of gas whether the pressure is being increased or decreased. These observations of Cook suggest a slow adsorption that is more or less reversible as a possible cause of the variation in surface tension, though any such slow desorption was not detected in the present work.

§ 7. CONCLUSIONS

The conclusions reached in this paper may be summarized as follows. Adsorbed carbon dioxide or hydrogen to the extent of a monomolecular layer is retained by the mercury surface on evacuation. The adsorption is readily observed when the mercury surface is formed in a gas but not when the gas is admitted to a surface which has been formed in a vacuum. It seems more probable that this is due to something acting as a contamination than to some inherent property of the mercury causing changes in the transition layer at the surface. If more than a single layer of gas molecules condenses on the surface the subsequent layers are lost on evacuation.

Though the mercury surface, from its uniformity and definite area, should be ideal for quantitative work on gas-adsorption on a metal, the phenomena observed are at present too complex to be embraced in a single theory. For processes occurring during the actual formation of the surface it is probable that the theory of adsorption at liquid surfaces applies, but this sheds little light on processes occurring after the surface has come to rest.

§ 8. ACKNOWLEDGMENTS

The author's thanks are again due to Prof. Kerr Grant for helpful discussion and to Mr R. H. Oliphant for his skill in constructing the apparatus in such a way that it could withstand the severe strains imposed on it.

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ERRATA

"A negative-resistance device and its application to harmonic analysis", by C. W. OATLEY, M.A., M.Sc., vol. **47**, p. 471.

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"The effect of pressure on supersonic dispersion in gases", by W. RAILSTON, M.Sc. and E. G. RICHARDSON, B.A., D.Sc., Ph.D. Remarks in discussion by Prof. E. N. DA C. ANDRADE, F.R.S., vol. **47**, p. 777.

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A NEGATIVE-RESISTANCE DEVICE AND ITS APPLICATION TO HARMONIC ANALYSIS

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ABSTRACT. A description is given of a negative-resistance device which is very similar in principle to the kallirotron amplifier described by L. B. Turner. It is shown that when this device is used to decrease the effective resistance of a tuned circuit no appreciable distortion of the resonance curve of the circuit is produced. A method is given whereby the effective resistance of the tuned circuit may quickly be adjusted to any predetermined value.

§1. GENERAL PRINCIPLES

NEGATIVE-RESISTANCE devices have found many interesting applications since the introduction of the dynatron by Hull in 1918. Shortly after this date Turner published an account* of a circuit, termed by him the "kallirotron amplifier", in which a negative-resistance effect was obtained without the aid of secondary electron emission. About five years ago the present author, who at that time had not seen Turner's paper, devised a very similar circuit which has since been used in the manner described below. In view of the facts that Turner's paper is not very generally accessible and that the kallirotron differs in certain practical details from the author's circuit, a brief description of the latter will first be given.

Consider the circuit of figure 1. The condensers C_1 and C_2 are inserted merely for the purpose of preventing the flow of direct current and we suppose them to be so large that their reactances are negligible. The resistances R_1, R_2 and R_3 are so large that currents flowing through them may be neglected in comparison with the anode current of the valve V_2. Suppose an alternating e.m.f. of magnitude E to be applied between the terminals A and B. Then some fraction bE of the e.m.f. is applied between grid and filament of V_1, where b is a constant lying between 0 and 1 and depending on the setting of the potentiometer R_1. Since R_2 is large, the e.m.f. applied between the grid and filament of V_2 will be nearly equal to $-\mu bE$, where μ is the amplification factor of V_1. If the mutual conductance of V_2 be k the alternating component of current flowing through this valve will be $-\mu kbE$. Since currents in other branches of the circuit are negligible in comparison with this, we have the result that the application of the e.m.f. E gives rise to a total current $-\mu kbE$. Thus, looked at from the terminals AB, the circuit is equivalent to a resistance $-1/\mu kb$ so far as alternating currents are concerned. Taking as typical

R_1, R_2,

E

b

μ, k

* L. B. Turner, *Radio Review*, **1**, 317 (1920).

values $\mu = 25$, $k = 1$ mA./V., and remembering that b can vary between 0 and 1, we see that the value of the negative resistance can be made to lie anywhere between -40 and $-\infty\ \Omega$.

Comparing the present arrangement with a dynatron we see that both require the circuit in which they are connected to offer a passage to direct current. With regard to frequency-range the present device will operate successfully from about 20 c./sec. to 100 kc./sec. At higher frequencies inter-electrode capacities become important; with care the upper limit might be extended, but experiments in this direction have not been carried out. Below 20 cycles per second the blocking condensers have to be made inconveniently large, but it is possible to use battery

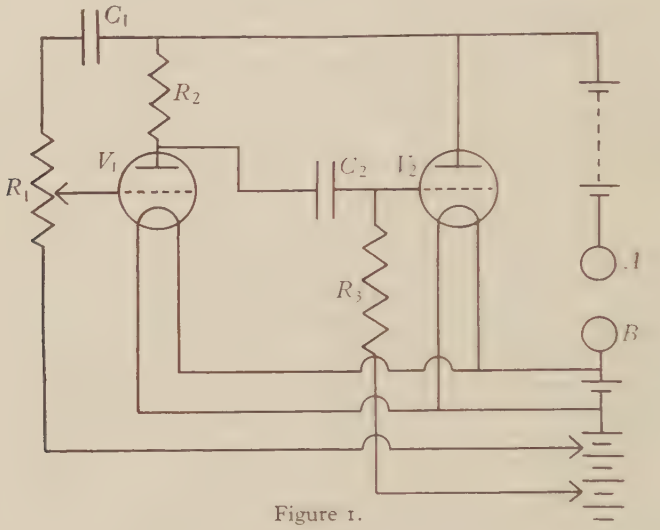

Figure 1.

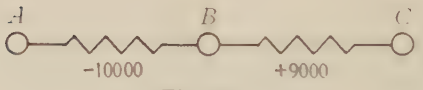

Figure 2.

coupling instead. On the whole, however, the dynatron is to be preferred if the range of frequencies to be covered is very wide. With regard to stability of characteristics, the present device has the great advantage that, unlike the dynatron, it does not depend upon the somewhat erratic phenomenon of secondary emission, and there is no reason why it should vary in performance any more than does a simple low-frequency amplifier.

Another very important advantage over the dynatron lies in the range of values of negative resistance which can be obtained. With ordinary receiving valves it is difficult to obtain by the dynatron method resistances lower than some 10000 Ω. in absolute value, whereas with the present device negative resistances as low as $-40\ \Omega$. are easily possible. Admittedly one can always obtain a low value of negative resistance by placing a positive resistance in series with a dynatron, but

the practice is not to be recommended. Thus in figure 2 if we place a positive resistance of 9000 Ω. in series with a negative resistance of −10000 due to a dynatron, the effective resistance between A and C is −1000 Ω. However, if the maximum permissible voltage across the dynatron be V, the voltage between A and C must not exceed $V/10$ and this limitation may be serious. Furthermore, if the resistance of the dynatron should change accidentally by 1 per cent, the resistance between A and C would change by 10 per cent.

One final advantage of the present device is the ease with which the magnitude of the negative resistance can be changed merely by varying the setting of the potentiometer R_1.

§ 2. APPLICATION TO HARMONIC ANALYSIS

The simplest type of electrical harmonic analyser is that in which the various components of a complex current wave are selected one by one by means of a sharply tuned resonant circuit and measured with a thermoammeter or other suitable device. In practice the chief difficulty is to obtain circuits of sufficiently low resistance to enable the various components of current to be effectively separated. However, this difficulty can be overcome by the use of the negative-resistance device described above.

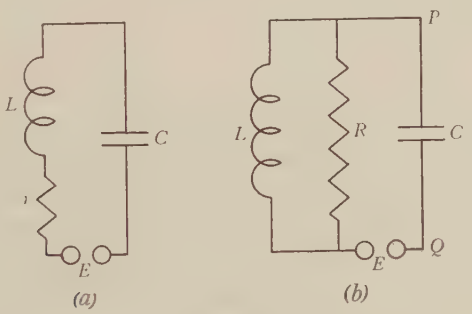

Figure 3.

To a first approximation, the resonant circuit of figure 3(*a*) may be replaced by the equivalent circuit of figure 3(*b*), where $R = L^2\omega^2/r$ and the approximation will be sufficiently good for our present purpose provided that $L\omega/r$ be not less than 10. Coils for which this is the case are not difficult to construct except at the lowest acoustic frequencies. If now we connect the points P and Q, figure 3(*b*), to the terminals A and B of the negative resistance circuit of figure 1, we shall place a negative resistance, R' say, in parallel with R. The resulting equivalent shunt resistance of the tuned circuit will be $RR'/(R+R')$, and theoretically this can be made as large as we please by suitable choice of R'. The practical limit is set by the tendency of the circuit to oscillate spontaneously.

The above arrangement is, of course, simply one method of applying reaction to a tuned circuit. Its advantage over most other methods lies in the ease and ac-

curacy with which the reaction can be controlled, the freedom from any distuning effect due to reaction, and in the fact that it can be used with circuits tuned to quite low frequencies.

§ 3. PRACTICAL DETAILS

If instability is to be avoided, the useful range of values of negative resistance will be from $-R$ to $-\infty$, and in most cases R will not be less than about 10000 Ω. If the circuit of figure 1 be used as it stands, the whole useful range of variation of the negative resistance will be covered by a very small movement of the potentiometer slide, and fine control will be impossible. The minimum obtainable value of negative resistance could be increased to 10000 Ω. by reducing the values of R_1, R_2, or R_3, but such methods are objectionable because they amount to placing a positive resistance in parallel with the negative one. In such a case a small accidental variation of either the positive or the negative resistance would cause a much larger percentage variation of the combination of the two. A better method of increasing the minimum value of negative resistance is to place a suitable resistance in the anode circuit of V_2 and another between R_1 and C_1. If the first be made several times as large as the slope resistance of V_2 it will greatly reduce the effect of any accidental variation of this quantity (due, for example, to fluctuation of battery voltages), while the second resistance in series with R_1 can be chosen so that the requisite range of values of negative resistance is just covered by the full movement of the potentiometer slide.

§ 4. EXPERIMENTAL RESULTS

Since a harmonic analyser should be capable of giving quantitative results, it is necessary to ascertain whether the addition of the negative-resistance device to a tuned circuit causes any distortion of the resonance curve apart, of course, from the change to be expected from a decrease in the effective resistance of the circuit. To test this point a series resonant circuit consisting of a coil having an inductance of 1 H. and a condenser of capacity 0·0397 μF. was set up. A small e.m.f. of the correct frequency for resonance, about 800 c. sec., was induced in the coil and the p.d. across the condenser was measured with a valve voltmeter. The negative-resistance device, connected in parallel with the coil, was adjusted until the circuit was sharply tuned. A variable air condenser connected across the main condenser enabled the tuning of the circuit to be varied over a small range of values, and in this way data for a resonance curve were obtained. The results are shown in the table, where the figures in the first column refer to settings of the air condenser and those in the second to the readings of the valve voltmeter. The values in the last column are calculated from the formula for a series-tuned circuit. In applying this formula we need to know the effective resistance of the circuit and also the e.m.f. induced in the coil. These two quantities are calculated from the observed maximum and minimum readings of the valve-voltmeter, marked with an asterisk in the table. It will be seen that the remaining voltmeter readings are in good

agreement with the calculated values. In this particular example the effective resistance of the circuit is found to be about 6·7 Ω., corresponding to a voltage-magnification at resonance of 750, which is many times as great as would have been obtained without the use of the negative resistance.

θ	V (observed)	V (calculated)
69	40·0*	40·0
68	48·0	48·7
67	61·0	59·1
66	76·0	73·4
65	91·0	88·3
64	103·0	101·5
63	110·0*	110·0
62	108·0	108·0
61	98·0	101·0
60	85·0	87·7
59	72·0	72·7
58	57·0	58·5
57	48·0	48·7
56	40·0	39·8

§ 5. DETERMINATION OF THE EFFECTIVE RESISTANCE OF THE CIRCUIT

When a series-tuned circuit is used in conjunction with the negative-resistance device, the effective circuit resistance can always be found by the method described above, but this would be too tedious when the circuit was being used to separate the various components of a complex voltage wave, since the effective resistance would alter every time the circuit was tuned to a fresh component. The following more direct method was therefore tried.

If the negative resistance be gradually decreased, a point will be reached where the circuit is on the verge of spontaneous oscillation. In practice this point is quite clearly defined and obviously corresponds to an effective circuit resistance of zero. If, having brought the circuit to this state, we now insert an extra resistance P in series with the inductance, then P should be the total effective circuit resistance and can be chosen to have any desired value. Preliminary tests of this method gave unsatisfactory results and the trouble was eventually traced to the fact that the resistance P is traversed by the direct current flowing in the negative resistance device and the addition of P therefore changes the value of the negative resistance. The difficulty was overcome by placing P in series with the condenser instead of with the inductance.

As a quantitative test of this method the following experiment was carried out. The tuned circuit (inductance 1 H., capacity 0·1 μF.) was brought to the verge of oscillation by adjustment of the negative resistance and a resistance of 1 Ω. was then connected in series with the condenser. An e.m.f. of the resonant frequency was next induced in the coil and adjusted in magnitude till the valve voltmeter showed a full-scale reading. The resistance in series with the condenser was then increased

to 2 Ω. and, as a result, the voltmeter reading dropped to 0·51 of its previous value. The experiment was then repeated, the resistance in series with the condenser being at first 2 Ω. and subsequently increased to 4 Ω. This time the first voltmeter reading was exactly twice the second. Two further steps gave the same result and brought the nominal effective circuit resistance up to 16 Ω. The actual effective circuit resistance was then determined by the distuning method and found to be 15·6 Ω. The difference between these two values is probably not greater than the experimental error in the second determination. It thus appears that the method described above provides a satisfactory means of adjusting the effective circuit resistance to any desired value.

DISCUSSION

Dr L. Hartshorn asked whether the same circuit would serve for the whole range of audio frequencies.

Dr A. B. Wood asked whether the negative resistor contained any reactive component; if so, it might make a good oscillator.

The Author replied that the apparatus worked satisfactorily over the range from 100 to 10,000 c./sec. The negative resistor contained only a negligible reactive component if the condensers C_1, C_2 were large enough, but could be converted into a good oscillator for the range from 50 to 10^5 c./sec.

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A NEW SELENIUM-SULPHUR RECTIFIER PHOTOELECTRIC CELL

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ABSTRACT. The paper describes a method by which a new selenium-sulphur rectifier photoelectric cell may be constructed, and gives the results of the first part of a full investigation of the physical behaviour of these new cells. The results are related to the details of construction of the cell, so as to show how far they support the theories of A. H. Wilson and of Frenkel and Joffé. A number of simple equations expressing the performance of the cell have been deduced.

§ 1. INTRODUCTION

The comparatively recent appearance of the rectifier or *Sperrschicht* photoelectric cell has recalled into prominence the contact photoelectric phenomena observed by Uljanin.[1] Uljanin annealed a thin layer of selenium between two plates of glass; the glass surfaces in contact with the selenium were covered with semitransparent metal films which formed the electrodes of the cell. He found that when the selenium was illuminated through one of the semitransparent metal films the cell generated an electromotive force; with sunlight the open-circuit e.m.f. generated amounted to 0·12 V. The illuminated electrode was the negative pole of the cell.

This cell should not be confused with the well-known photoconducting selenium cell, which shows an increase of conductance on illumination. The photoconducting cell does not generate an e.m.f. on illumination and is always used with an external source of e.m.f.

The modern Sperrschicht cell is said to consist of a metal plate coated with a thin layer of some semiconductor, the upper surface of which is covered with a very thin film of metal. The metal plate and the metal film form the electrodes of the cell and are directly connected to the terminals of a current-measuring instrument. Precise details of construction do not appear to have been published either in scientific journals or in patent specifications. Such information as is available is not sufficient for the construction of a cell with a sensitivity comparable with the known sensitivities of cells on the market.

The work described in the present paper was originally undertaken in order to develop a simple and accurate instrument which could be used for measuring the distribution of illumination in small-scale model rooms. The original intention was to use one of the well-known forms of Sperrschicht cell; but it was immediately apparent that these would be unsatisfactory for the measurement of diffused light, owing to their marked decrease of sensitivity with increase of angle of incidence.

Accordingly it was decided to investigate the method of construction of such cells in order, if possible, to effect an improvement in this respect. A simple method was eventually devised which enabled compensation for this decrease in sensitivity to be made to within 3 per cent of the required sensitivity for angles of incidence from 0 to 85 degrees; the results of this work will be the subject of a separate publication. The present paper gives the results of the first part of a full investigation of these new cells.

In a recent short note[2] the author has described briefly a method of constructing a new selenium-sulphur rectifier photoelectric cell. The description is now given for the first time in sufficient detail, and the construction of the cell is related to the results obtained, so as to show how far these results support the theories of A. H. Wilson, and of Frenkel and Joffé. A number of simple equations expressing the performance of the cell have been deduced.

§ 2. MODERN THEORY

A short qualitative discussion of the theoretical treatment given by certain writers of the rectifying properties of a semiconductor metal contact will serve to indicate the general nature of the problem, and to prepare the way for the interpretation of the experimental results described in this paper. A list of original papers is given for reference[3].

2·1. *The contact gap.* It is always assumed at the outset that in the system metal/semiconductor metal the two contacts are dissimilar; that at one contact the bounding surfaces of the metal and the semiconductor are separated by a small gap δ of definite width δ, while at the other contact the separation of the bounding surfaces is relatively so small that this contact can have none of the properties of the first. Thus with this assumption it is only necessary to consider the first of these contacts.

It is not possible to say definitely what is the nature of the surface of the semiconductor that in contact with a metal will yield a high-resistance interface; experimentally, however, it is known that certain methods of treatment give high-resistance contacts, and that other methods do not. Schottky and Deutschmann's measurement of the electrostatic capacity of the transition layer showed that δ, in the cells used by them, was of the order of the mean free path of electrons in ordinary electronic conductors. But little or nothing is known of the actual nature of this transition layer. That it is not a vacuum, or a layer of gas, is admitted generally, although in its properties it can be regarded as being mathematically equivalent to a vacuum. N. R. Campbell and A. H. Wilson adhere to the view that the bounding surfaces of the metal and the semiconductor are separated by an insulating film of the semiconductor freed from all conducting impurities. So long as the thickness δ of this film is smaller than the mean free path of an electron in the material of the film, the film will be exactly equivalent to a layer of vacuum with a reduction, depending upon the dielectric constant of this insulating film,

of the height of the potential-energy mountain, which results from the image-force effect, between the surfaces of the semiconductor and the metal.

2·2. *Mathematical model of semiconductor.* According to A. H. Wilson's treatment, all electrons in the semiconductor at absolute zero of temperature are in what may be called bound states. At any other temperature a few electrons are thermally excited into energy states in which they can conduct. The mean value of the potential energy of these electrons, regarded as nearly free, is represented by the energy level W_2, figure 1. Wilson then deals with the case of a lattice possessing atoms of an impurity, each atom having a single electron in a discrete state of energy W_1. The level W_1 lies below the level W_2 but above the highest occupied energy level, W, of electrons possessed by atoms of the pure semiconductor, so that electrons from the level W_1 can make the transition to the level W_2 more easily than electrons from the level W. The conduction electrons are thus entirely derived from impurities. His equations hold so long as the number of impurities is less than 10^{17} per unit volume but still sufficiently large to mask entirely the natural conductivity of the semiconductor. With these premises A. H. Wilson determines the distribution function for the impurity electrons.

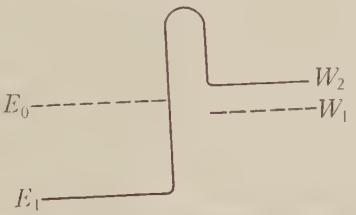

Figure 1. Potential-energy states at boundary between metal and semiconductor (Wilson).

Frenkel and Joffé on the other hand make use of the Maxwellian form of the Fermi-Dirac statistical expression for a small free-electron concentration in the semiconductor. They find, however, that for any reasonable value of the free-electron concentration, of the order of 10^{17} per cm.^{3}, the free energy of an electron turns out to be negative and at 300° K. is of the order of $-0{\cdot}15$ electron-volt. The final equations deduced by Frenkel and Joffé and by Wilson to express the rectifying properties of a semiconductor/metal contact are not essentially different in so far as their application to any practical case is concerned.

2·3. *The transmission coefficient of the contact gap.* When the steady state has been reached for the flow of electrons in any given direction through and normal to the contact, the charge-distribution and the current may be obtained from a solution of the Schrödinger wave equation. The solution will in general show two terms, one representing an electron wave travelling in the positive direction—the incident wave—and the other representing a wave proceeding in the negative direction—the reflected wave. The ratio of the intensity of the reflected wave to that of the incident wave is the reflection coefficient R of the contact gap; while the ratio of the intensity of the transmitted wave to that of the incident wave is the transmission coefficient D. Obviously $D+R=1$. It is seen, therefore, that the

contact resistance results from the reflection of electrons at the assumed transition layer between the bounding surfaces of the metal and the semiconductor; on the other hand the bulk resistance of a solid arises from the interaction of the electrons with the elastic vibrations of the lattices. The transmission coefficient, and hence the resistance of the contact gap, depends upon the applied electric field in the gap.

2·4. *Equations to express the rectifying properties of contact.* In both cases the problem has been made one-dimensional, doubtless to simplify the mathematical treatment; consequently in the formulation of the results for any actual cell some modification of the equations so derived will be necessary. Figure 1 gives a one-dimensional picture of the potential states at the boundary between a semiconductor and a metal. The continuous curve represents the potential energy of conduction electrons, the left- and right-hand horizontal portions corresponding to the potential energies in metal and semiconductor respectively. Sommerfeld and Peirl's model of a metal is used, the valency electrons being considered as nearly free. The mean E_1 value of the potential energy of a valency electron is represented by E_1; its position relative to W_2, defined in 2·2, is determined from the condition of equilibrium. The level E_0 in the metal corresponds to the maximum critical energy of the Fermi distribution; E_0 is approximately equal to the maximum kinetic energy of an electron at absolute zero of temperature, and for most metals is of the order of 10 electron-volts. It is not necessary for the energy of an electron to be raised above the surface-potential jump in order to cross the surface into the transition layer, represented in figure 1 by a potential hump which, in the theoretical treatment, is assumed to be of rectangular form. Electrons can, according to the wave-mechanical treatment, pass through the hump if it is not too high or too broad. An analogous case is the passage of light-waves from glass into air and into another piece of glass, even at angles greater than that of total internal reflection, when the intervening air film is sufficiently thin.

Electrons passing from the metal to the semiconductor must acquire kinetic energies of not less than W_2; electrons passing from the semiconductor to the metal must also be raised by thermal excitation to the level W_2, in order to become conduction electrons in the semiconductor. If there is no potential difference applied between the metal and the semiconductor they will assume a contact difference of potential in the equilibrium condition for zero field, when equal numbers of electrons flow in either direction. The equations of A. H. Wilson show that the current from the semiconductor to the metal is equal to the current from the metal to the semiconductor only when E_0 lies approximately half-way between W_1 and W_2. This is, then, the equilibrium condition for zero field, the position of E_1 with respect to W_2 being determined.

If now the potential of the metal be raised by a small quantity eV less than $(W_2 - E_0)$, the effect of the applied field will be to change the transmission coefficient and to increase E_1 and E_0 by eV, while leaving W_2 unaltered. It is no restriction to consider W_2 as invariable, since differences only in these quantities are of significance. The raising of E_0 above the equilibrium position for zero field will be compensated by an increased flow of electrons from the metal to the semiconductor, while

leaving unchanged the current in the reverse direction. The difference between these two currents gives the net current from the metal to the semiconductor. If the subscripts a and b denote the semiconductor and the metal respectively, this net current ${}_bI_a$ is given by

a, b
${}_bI_a$

$$ {}_bI_a = \alpha \{\exp(-\beta V)\} \{\exp(eV/kT) - 1\} \quad \ldots\ldots(1), $$

where α is a constant depending upon T and upon the magnitude of the contact resistance at zero applied voltage, e the electronic charge, k Boltzmann's constant, T the absolute temperature, and β a constant determining the dependence of the transmission coefficient on V.

α
e, k
T, β

If the potential of the metal is lowered by the same quantity V, the net current from the metal to the semiconductor is similarly determined and is found to be negative. The current equation now becomes

$$ {}_aI_b = \alpha \{\exp(\beta V)\} \{1 - \exp(-eV/kT)\} \quad \ldots\ldots(2) $$

for the reverse direction.

Frenkel has deduced a value $\beta = 1{\cdot}5$.

It can be seen from equations (1) and (2) that the effect of the applied field on the transmission coefficient of the gap always tends to nullify the rectifying effect; this follows from the fact that a decrease in $(W_2 - E_1)$ makes the potential hump higher and decreases the transmission coefficient.

2·5. These equations may now be applied to the case where light falls upon a rectifier cell in the absence of any applied voltage. The metal in contact with the semiconductor is now sufficiently thin to transmit visible radiation. A number of electrons per second, extracted by light of energy F from the semiconductor, will cross the transition layer and enter the metal, this number being directly proportional to F. This electron current, from semiconductor to metal, will increase the contact potential difference between a and b by an amount V', which in its turn will produce a current in the reverse direction. If there is no other connexion between a and b, V' will reach a stationary value in the equilibrium condition when the electron-flows in the two directions are equal. If i_p denotes the primary photoelectric current and i_r the reverse current, equation (1) gives

F
V'
i_p
i_r

$$ i_p = i_r = \alpha \{\exp(-\beta V')\} \{\exp(eV'/kT) - 1\} \quad \ldots\ldots(3). $$

Since i_p is directly proportional to the light-flux F, equation (3) may be written

$$ F = \lambda \{\exp(-\beta V')\} \{\exp(eV'/kT) - 1\} \quad \ldots\ldots(4), $$

where λ is a new constant. Equation (4) represents an important relation between the light flux and the voltage developed on open-circuit in a rectifier photoelectric cell *in the absence of any applied voltage*. In § 5 will be found examples of its application to the results from a number of specific cells, from which it will be seen that the measured values of the constant β may be very different from the value 1·5 deduced by Frenkel in his one-dimensional treatment. Departures from equation (4) are discussed in § 5.

λ

§ 3. DETAILS OF CONSTRUCTION OF SELENIUM-SULPHUR RECTIFIER PHOTOELECTRIC CELLS

3·1. The cells referred to in § 1 were originally made from steel discs ground flat on one surface, 5·1 cm. in diameter, and 0·8 mm. thick, by coating them with a selenium-sulphur mixture. After the annealing of the layer a thin film of silver was sputtered on to the surface of the mixture. Experiments were continued with these steel discs. Discs of zinc, brass, copper, tin and aluminium also were used, but no really successful cell was obtained; the failure appears to be due to the difficulty of obtaining a small contact gap between the selenium-sulphur film and the surface of these metals. The sulphur was added to the selenium because of the extreme difficulty of coating an iron plate with a thin, uniform, and continuous film of selenium alone; the transformation of the vitreous form of selenium into the grey, metallic variety is attended by a considerable diminution in volume, and this tends to cause rupture at a contact surface and to introduce microscopic cracks and air cavities throughout the material. Thin annealed films of selenium-sulphur are almost entirely free from such mechanical imperfections.

Twenty cells were made with mixtures of selenium and sulphur in various proportions. Pure flowers of sulphur, varying by unit steps from 1 to 10 per cent of the total weight, was added to molten selenium to give ten different mixtures of selenium and sulphur; two cells were made with each mixture. There were, however, no marked variations in sensitivity, but it was found that when the added quantity of sulphur was less than 5 per cent of the total weight the difficulty of obtaining a uniform and continuous film on the iron disc remained. Accordingly subsequent investigation was concentrated upon mixtures containing 10 per cent of sulphur by weight. This mixture melted at approximately 185° C. The melting point of pure selenium is 220° C. The solvent (selenium) separated on cooling, and appeared to be embedded in a matrix consisting of a eutectic mixture of sulphur and selenium. A comparison of the X-ray diffraction patterns given by the pure selenium and by the selenium-sulphur mixture showed that the sulphur atoms entered the selenium lattice; this resulted in a small change in the dimensions of the selenium lattice. The lines given by the selenium-sulphur mixture were sharper than those given by pure selenium; this indicates that the crystals were better developed in the selenium-sulphur mixture than in pure selenium. The selenium used has been described as pure, because consistent success in manufacture was ensured only when the purest selenium available was used. In § 1 Wilson's theory of the rectifier cell was discussed; his treatment depends upon the presence in the semiconductor of impurity sufficient in amount to mask entirely the natural conductivity of the substance. In this work, however, the selenium used was obtained from Germany and was stated to be 100 per cent pure according to chemical analysis; very small traces of metals could be found spectroscopically, but it is doubtful whether these traces of metal represent a sufficient amount of impurity to accord with Wilson's theory.

3·2. *The coating of the iron discs.* Flat circular brass plates, 8 cm. in diameter, were recessed to take one steel disc; plates recessed to depths of 1·2 mm., 1·0 mm. and 0·85 mm. approximately were employed. A brass plate holding one steel disc with its ground surface uppermost was maintained at a temperature of approximately 200° C., while the steel disc was coated uniformly with the molten mixture by means of a flat piece of steel maintained at the same temperature, the surface of the coating being made flush with the surface of the brass plate. With the coated disc in position the brass plate was then cooled rapidly, and while the selenium-sulphur mixture was still plastic its surface was rolled smooth by means of a polished silver-steel roller to give a film of approximately uniform density and thickness. During the rolling, the ends of the roller were in contact with the flat edge of the brass plate. Selenium-sulphur films having approximate thicknesses of 0·4, 0·2 and 0·05 mm. were thus obtained. A slit cut in the edge of the brass plate facilitated the removal of the coated iron disc after rolling.

3·3. *Annealing of selenium-sulphur films.* In the annealing experiments an electric oven with thermostatic control was employed. The temperature was measured by means of a mercury-in-glass thermometer. Experiments on the annealing of the vitreous selenium-sulphur mixture were carried out over a range of temperature of from 140° C. to 185° C. for periods varying from 30 minutes to 30 hours. The results indicate two distinct stages in the annealing. For example, when a coated disc is maintained at 160–165° C. over a period of 3 hours the transformation to the grey, metallic variety takes place; but the surface of the selenium-sulphur still preserves a smooth glazed appearance and has a violet-grey colour by reflected light. The conductivity is very low. If this period of time is extended, or if the annealing is begun at a higher temperature, say 170–175° C., a further change takes place. The surface becomes neutral grey in colour and has the appearance of having a porous structure; its conductivity is relatively very much higher. The annealing required to produce the necessary allotropic change needs careful attention; no success at all is obtained with an unannealed selenium-sulphur film. The annealing determines not only the conductivity of the semiconductor but also the state of the surface. It has been shown that two quite different types of surface can be produced, but there is no sudden change from one type to the other in the annealing. In fact between the two extremes, which have been named type A and type B, many curious results may be obtained. For the pure selenium and pure sulphur used in these experiments, the conditions of annealing can be specified approximately as follows:

Type A: 3 hours at 160–165° C.

Type B: 6 hours at 170–175° C.

The conditions depend upon the purity of the elements used and must not, therefore, be rigidly applied to every new supply of selenium and sulphur. The determination of these types was assisted by resistance-measurements at a definite applied voltage.

3·4. *Sputtered metal films.* The specimens were sputtered one at a time in a bell jar waxed to a brass plate by means of a wax of very low vapour pressure.

The source of supply was a 2000-V. 0·5-A. direct-current generator. The voltage between the electrodes was measured by means of an electrostatic voltmeter, and a milliammeter was connected in series with the supply. All experiments were carried out with a current-density of 10^{-4} A. cm.^{2} at 1400 V. with a vacuum to give a dark space approximately 3 cm. in length. The specimens were placed at the edge of the negative glow, i.e. just outside the Crookes dark space. An aluminium ring with an inside diameter of 4·9 cm. was placed on the selenium-sulphur surface so as to leave an unsputtered rim of selenium about 1 mm. wide.

Sputtering was tried with the following metals: cadmium, lead, tin, zinc, copper, nickel, silver, gold, platinum and brass. The last apparently sputters as brass. Iron and aluminium do not sputter appreciably.

Successful cells were not obtained with cadmium, lead, tin or zinc, principally because of the oxidation of the cathode; thin films of oxide appeared on the surface of the semiconductor, giving interference colours. The formation of selenides of these low-melting-point metals was also suspected. Attempts made with copper, nickel and brass were only partially successful; oxidation of the cathode occurred, but to a much smaller extent. Accordingly, all subsequent experiments were restricted to sputtered films of gold, silver and platinum.

§ 4. DETAILS OF APPARATUS AND METHODS OF MEASUREMENT

4·1. In all the illumination measurements a 1000-W. 100-V. gas-filled projection lamp operating at 50 V. and giving a candlepower of 216·5 candles in a known direction perpendicular to the plane of the filament was used on a 3-metre photometer bench. The colour temperature of the lamp at 50 V. was given as 2360 K.

A holder for the selenium-sulphur photocell, containing eight fine-wire brush contacts arranged equidistantly round the edge of the sputtered metal film and pressing lightly on it, was made; contact with the back of the iron base of the cell was made by a flat-nosed metal screw. By means of the holder each cell could be easily and accurately mounted on a photometer carriage. A vernier potentiometer was used to measure the p.d. across various standard resistances, 1, 10, 100, 1000, 10,000 Ω. and 1 MΩ., in series with the cell. The maximum range of illumination was from 0 to 225 foot-candles. A holder for an adjustable iris diaphragm was also constructed; in those experiments in which the iris diaphragm was employed, the diaphragm was mounted and centred in front of the cell in a plane parallel with the plane of the cell and at a distance of 1 cm. from its surface.

In the determination of the spectro-photoelectrical sensitivity each cell was connected in series with a galvanometer of resistance 15 Ω. and of sensitivity 2000 mm. μA. at 3 metres. A constant-deviation spectrometer was employed with an Adam Hilger linear thermopile made for the spectrometer. No slit-width correction was used. The wave-length band at 5900 A. was approximately 50 A. No precautions were taken to allow for stray light in the spectrometer. Apart from correction for these possible sources of error, the results give the spectro-photoelectrical sensitivity of these cells.

4·2. In the course of this work about three hundred cells were constructed; considerable experience with regard to the general behaviour of these cells under illumination was thus gained. It will be appreciated that with the many possible variables in construction the reproduction of cells with precisely similar properties is a matter of considerable difficulty. This is not surprising in view of the fact that surface effects can still only be treated phenomenologically. For special purposes exactly similar cells may be produced if during the sputtering process the response of the cell is compared with that of a completed cell by illuminating the cell under construction to a known intensity through the bell jar. The sputtering may be discontinued when the two cells show the same response over a small but definite range of illumination.

The precise measurement of the response of a cell presents, of course, no difficulty. Where comparisons are made between the results obtained from cells, among which there are known variations in the controllable variables in construction, the results given apply to cells whose response represents the average response obtained to an accuracy of about ± 1 per cent.

It will be necessary to comment on certain specific cells in § 5; these cells have been numbered for reference purposes, and are specified in table 1.

Table 1

Cell no.	Approximate thickness t of selenium-sulphur film (mm.)	Type of surface	Sputtered metal	Time of sputtering (min.)
1	0·4	B	Gold	23
4	0·2	B	Silver	60
5	$0{\cdot}0_5 < t < 0{\cdot}1$	A	Platinum	4
6	0·2	A	Platinum	4
7	0·4	B	Platinum	12
9	0·4	B	Platinum	15
10	0·4	B	Gold	30
11	$0{\cdot}0_5 < t < 0{\cdot}1$	A	Platinum	4

§ 5. APPLICATION OF THEORY AND EXPERIMENTAL RESULTS

5·11. A complete rectifier photoelectric cell may be represented by the equivalent circuit given in figure 2, in which R_f denotes the effective resistance of the sputtered metal film, R_s the bulk resistance of the semiconductor, R_r the effective resistance of the transition layer measured from the metal to the semiconductor, and R_e the resistance of any external measuring instrument. When $R_e \to \infty$, i_r, the reverse current, becomes equal to i_p, the primary photoelectric current; but when R_e is finite, the reverse current is no longer equal to i_p, since some fraction of i_p will be transmitted in its original direction, and a current i_e depending upon the magnitude of R_e will flow in the external circuit.

Thus
$$i_e = i_p - i_r' \qquad \ldots\ldots(5),$$
where i_r' denotes the new value of the reverse current. On open circuit $i_e = 0$, and $i_r' = i_p \equiv i_r$.

If in any actual cell i_p is independent of R_e, the voltage developed across the transition layer must obviously depend upon R_e, which determines the value of i_r', and upon the value of R_e.

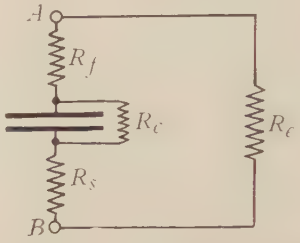

Figure 2. Circuit diagram of rectifier photoelectric cell.

The reverse current i_r' is given by equation (3), and since $i_r' = i_r$ when R_e is finite, the voltage developed across the transition layer is no longer equal to its open-circuit value V'. Let the voltage developed be V_0 for any given small value of R_e. If R_e is small the variation of the transmission coefficient with variation of V_0 may be neglected; i.e. R_e may be regarded as constant over a limited range of F, if R_e is small. Therefore from equation (1)

$$i_r' = \alpha \{\exp(eV_0/kT) - 1\},$$

or

$$V_0 = \frac{kT}{e} \log\left(\frac{i_r'}{\alpha} + 1\right) \qquad \text{.....(6).}$$

But if Ohm's law is assumed for the resistances R_f, R_s and R_e,

$$V_0 = i_e(R_f + R_e + R_s) \qquad \text{.....(7).}$$

Hence from equations (6) and (7),

$$\frac{i_e e(R_f + R_e + R_s)}{kT} = \log\left(\frac{i_r'}{\alpha} + 1\right) \qquad \text{.....(8).}$$

In (8) put $\frac{e}{kT}(R_f + R_e + R_s) \equiv A$. Then

$$i_r' = \alpha \{\exp(Ai_e) - 1\} \qquad \text{.....(9).}$$

The value of i_r' obtained from (9) may be substituted in (5), whence

$$i_e = i_p - \alpha \{\exp(Ai_e) - 1\}$$

$$= i_p - \alpha \left\{Ai_e + \frac{(Ai_e)^2}{\lfloor 2} + \frac{(Ai_e)^3}{\lfloor 3} + \ldots\right\}$$

or

$$i_e(1 + \alpha A) = i_p - \frac{A^2 \alpha i_e^2}{\lfloor 2} - \frac{A^3 \alpha i_e^3}{\lfloor 3} - \ldots.$$

$$\therefore\ i_e = \frac{1}{1 + \alpha A}\left\{i_p - \frac{A^2 \alpha i_e^2}{\lfloor 2} - \frac{A^3 \alpha i_e^3}{\lfloor 3} - \ldots\right\} \qquad \text{.....(10).}$$

From equations (5) and (10) it is seen that since i_p is directly proportional to F, i_e can never be accurately proportional to F. If the deviation from true proportionality is small when $R_e = 0$, and if R_f and R_s are small, and if B denotes a constant

in the proportionality of i_p to F, equation (10) may be rewritten to give to a first approximation the relation between i_e and F, namely

$$i_e \cong \frac{1}{1+\alpha A}\left\{BF - \frac{A^2\alpha B^2}{\underline{|2}}.F^2 - \frac{A^3\alpha B^3}{\underline{|3}}.F^3 - \ldots\right\} \qquad \ldots\ldots(11).$$

This equation holds for all the cells, both of type A and type B.

5·12. From equation (7) it is seen that

$$\frac{V_0}{i_e} = R_f + R_e + R_s.$$

Since $V_0 \neq V'$, this quotient cannot be determined experimentally owing to the impossibility of separating R_c, R_f and R_s for the purposes of measurement.

5·13. When $V' \leqslant 5$ mV., expansion of the exponential terms in equation (3) shows that with sufficient accuracy

$$i_p = \frac{\alpha e}{kT} V' \qquad \ldots\ldots(12),$$

or

$$V' = \frac{kT}{\alpha e} i_p = R_c i_p \qquad \ldots\ldots(13).$$

When V' is very small $R_c \cong R_c'$, the value of the contact resistance when $V' = 0$. Thus when $V' \to 0$, $R_c \to R_c'$ and in the limit

$$R_c' = \frac{kT}{\alpha e} \qquad \ldots\ldots(14).$$

From equation (13), $V' = 0$ when $R_c = 0$, and therefore in the case of a very good contact, defined by $R_c = 0$, no voltage is developed on illumination.

5·14. In view of the difficulty of determining without reference to the experimental work exactly what is given by the quotient of the measured open-circuit voltage and the measured short-circuit current for the same value of F, this quotient, often vaguely termed the "resistance of the cell", will be considered in § 5·4.

Table 2

Sputtered metal	Cell type	Time of sputtering (min.)	Open-circuit voltage developed at 224 foot-candles
Gold	B	15	0·01080
Gold	B	23	0·00500
Silver	A	8	0·08440
Silver	A	9·5	0·06730
Silver	A	10	0·06080
Silver	A	12	0·04730
Platinum	A	4	0·18062
Platinum	A	6	0·11230
Platinum	B	14	0·05520
Platinum	B	15	0·03280

5·2. *Variation of open-circuit voltage with intensity of illumination.*

5·21. Table 2 gives the voltage developed on open circuit at an illumination of

224·0 foot-candles by a number of cells sputtered for various times. For selenium-sulphur surfaces of the class A type, experiment has shown that the open-circuit voltage V'' for any given illumination increases with the time of sputtering up to a maximum after from four to five minutes. With further increase of the time of sputtering, V'' decreases for the same illumination; if the sputtering be continued beyond sixty minutes, V'' decreases rapidly to a very low value with increase of thickness of the deposited metal film, which eventually becomes opaque to light after several hours of sputtering. The initial decrease of the open-circuit voltage from its maximum with increase of the time of sputtering cannot be, however, attributed solely to increased absorption of light by the metal film. Equation (13) shows that V' decreases with decrease of R_s'; it is therefore probable that the time of sputtering determines not only the light-transmission of the film, but also the resistance of the contact formed with the semiconductor.

It is a matter of common experience in the molecular deposition of metals by sputtering that different types of surface receive different amounts of metal at the same voltage, current-density and pressure of vacuum, and in the same time. The B type of surface proves to be more receptive than the A type; but more important is the fact that it has proved impossible experimentally to form a cell with a B type of surface which can for the same illumination give as high an open-circuit voltage as that given by a cell of the A type. Therefore R_s' can never be as high for the B type as for the A type. In the latter case the transition layer may be of pure sulphur, which in the former may be partially or wholly removed by prolonged annealing at a higher temperature, which decreases the effective width of the gap δ between the semiconductor and the metal film.

5·22. The intensity of illumination E, varied by changing the distance of the lamp from the cell along a photometer bench, is directly proportional to the light flux F incident on the cell so long as the illuminated area of its surface remains constant. When the whole surface of the cell is illuminated, equation (4) may be rewritten to give the relation between V' and E, thus

$$E=\gamma\{\exp(-\beta V')\}\{\exp(eV'/kT)-1\} \qquad \ldots\ldots(4'),$$

γ, r where $\gamma=\lambda/\pi r^2$, r being the radius of the cell.

The experiments show that the equation (4′) holds for all cells of the A type when β is positive and of the order of 15.

For type A cell no. 5 at 300° K. the observed values of V'' for a range of illumination of from 25 to 200 foot-candles, figure 3, are represented to an accuracy of about 1 per cent by the equation

$$E=3{\cdot}41_2\{\exp(-15{\cdot}4V'')\}\{\exp(eV''/kT)-1\} \qquad \ldots\ldots(15).$$

The experimental value of β is therefore approximately ten times the value 1·5 theoretically deduced by Frenkel and Joffé. Table 3 shows at various illuminations the experimental values of V'' and the values calculated from equation (15) for this cell.

It will now be shown that the value of β for any cell depends upon the ratio of the illuminated area to the area within the circular collecting electrode.

5·23. Cell no. 11, of type A, was mounted with the adjustable iris diaphragm on the photometer bench as described in § 4. The smallest aperture available was first used, the incident illumination being varied by moving the lamp along the bench. With each opening two curves were plotted showing (1) open-circuit voltage against light-flux, (2) short-circuit current against light-flux. The diaphragm was opened to give a range of known areas of aperture, the diameter of each opening being measured.

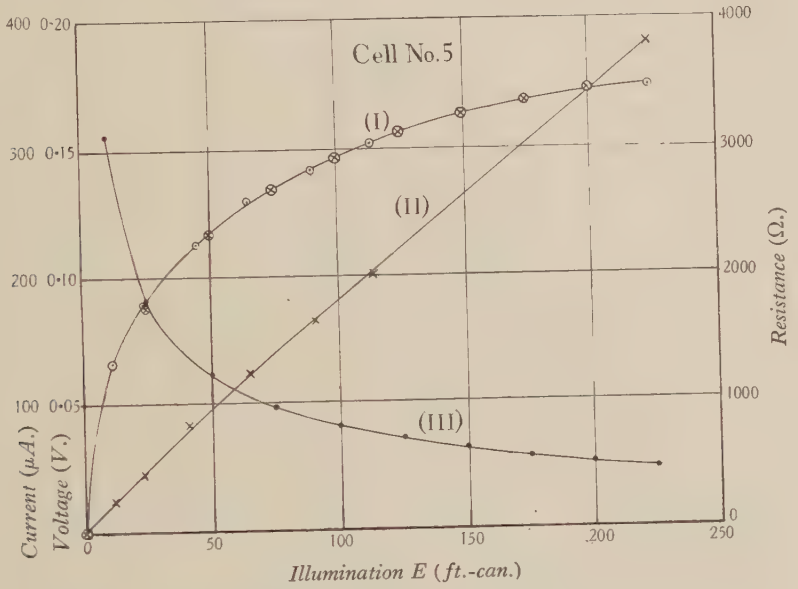

Figure 3. Illumination against (I) voltage, (II) current and (III) resistance.

Table 3

Illumination, E (foot-candles)	Open-circuit voltage, V', experimental values ($T = 300°$ K.)	Open-circuit voltage, V', values calculated from equation (15) ($T = 300°$ K.)
25	0·0885	0·0875
50	0·1165	0·1160
75	0·1340	0·1330
100	0·1460	0·1460
125	0·1560	0·1560
150	0·1630	0·1630
175	0·1680	0·1680
200	0·1730	0·1735

The value of β for each curve of open-circuit voltage against light-flux was then determined; these values are plotted against radius of aperture in figure 4. The short-circuit current sensitivity, expressed in μA. per lumen, was, for a given flux, found to be constant to within 2 per cent for any value of the aperture-radius; but the open-circuit voltage for the same flux increased with decrease of the radius,

figure 5, and it was found that the value of β depended upon the size of the aperture. Extrapolation to zero radius in figure 4 shows that for an extremely small radius

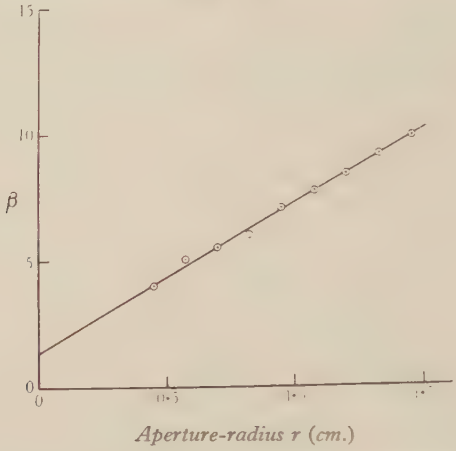

Figure 4. Curve relating β (equation 1) and radius of aperture of iris diaphragm.

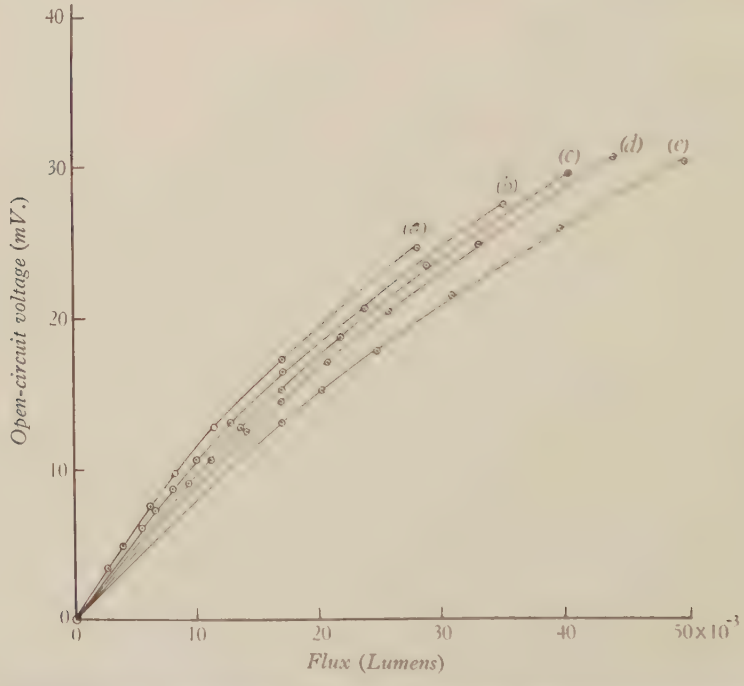

Figure 5. Curves showing open-circuit voltage against incident light-flux for the following values of aperture-radius (cm.): (*a*) 0·575, (*b*) 0·825, (*c*) 1·075, (*d*) 1·325, (*e*) 1·45.

(corresponding to Frenkel and Joffé's one-dimensional treatment) the experimental value of β would be equal to 1·4, which is quite close to Frenkel and Joffé's deduced value 1·5. This interesting result can be readily interpreted in terms of the effect

of space-charge limitation of current within the illuminated area of the metal film. The effect is, of course, absent in the one-dimensional treatment of Frenkel and Joffé.

The maximum open-circuit voltage measured for any given flux is limited by the number of photoelectrons collected by the circular electrode round the periphery of the sputtered film. In the absence of mechanical imperfections in the film there will be a radial distribution of electron-flow, but the electrons travel against a retarding potential dependent upon their initial position in the film and due to the space charge of electrons arising between them and the electrode. Electrons with insufficient kinetic energies will therefore return through the gap to the semiconductor.

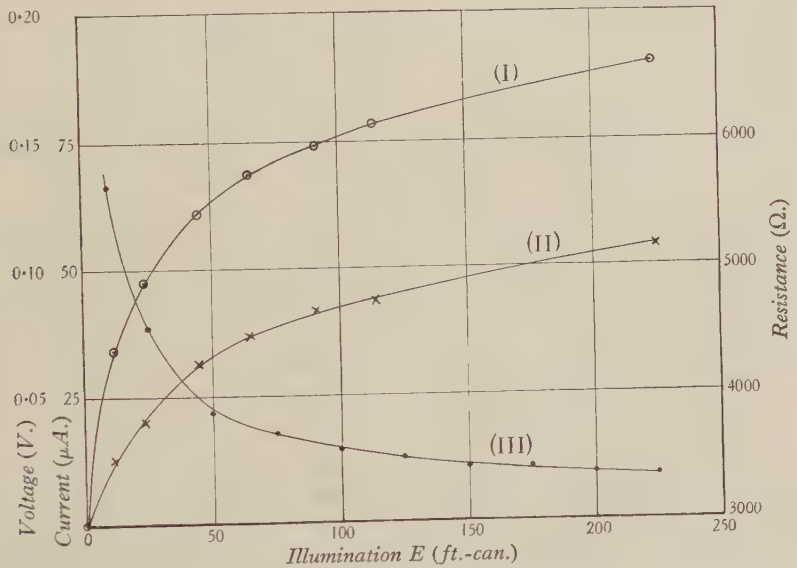

Figure 6. Curves showing illumination against (I) voltage, (II) current and (III) resistance for cell no. 6.

Equation (15) for class-A cell no. 5, with the whole surface illuminated, may be rewritten to give the relation between the measured open-circuit voltage V' and the primary photocurrent that arises from, and is directly proportional to, the illumination E. Thus

$$i_p' = B\{\exp(-15{\cdot}4V')\}\{\exp(eV'/kT)-1\},$$

where B is a constant.

But if Frenkel and Joffé's theoretical equation for the one-dimensional case held for this cell, then for any value V' of the measured open-circuit voltage the true primary photocurrent i_p'' collected by the circular electrode *in the absence of space-charge limitation* would be given by

$$i_p'' = \alpha\{\exp(-1{\cdot}5V')\}\{\exp(eV'/kT)-1\}.$$

It follows from these two equations that

$$i_p' \propto i_p'' \exp(-13{\cdot}9V') \qquad \ldots\ldots(16)$$

for any value V' of the measured open-circuit voltage. This relation between i_p' and i_p'' is similar in form to the corresponding relations in the theory of thermionic emission. The practical effect of this space-charge limitation is to make the transmission coefficient for electron-flow from semiconductor to metal appear to decrease more rapidly with V''. In other words, the contact resistance R_c from metal to semiconductor decreases more rapidly with increase of V'' than it would in the absence of a space-charge limitation of current, and the voltage shows a saturation effect. But as the illuminated area is reduced symmetrically about the centre of the cell the space-charge effect will be less important and the value of β calculated from the observations should fall, approaching the theoretical limit 1·5; this is in accordance with our observations.

5·24. When V' is below 10 mV. the omission of powers of V'' higher than the first (i.e. the assumption of a linear relation between V'' and E) in the expansion of the exponential terms in equation (15) produces a calculated error of less than 4 per cent. This is demonstrated experimentally in figure 7, where a curve relating voltage with illumination is given for cell no. 6 (type A) at very low illuminations, a 1 per cent neutral-tint filter being used in front of the cell.

5·25. *Cells of type B.* In contrast with cells of the A type, it is found that with the B type of surface it is possible by extending the time of sputtering to produce cells of a type represented by no. 4 which, while possessing current-sensibility of the same order as that of the A type, develop a voltage of only a few millivolts at 100 foot-candles, figure 8. The curve of open-circuit voltage against illumination for cell no. 4 is expressed by the equation

$$E = 399{\cdot}4\,\{\exp(-10{\cdot}7V')\}\,\{\exp(eV''/kT)-1\} \qquad \ldots\ldots(17).$$

In equation (17) when V'' is not greater than 10 mV., the illumination being 169 ft.-can., the omission of powers of V'' higher than the first in the expansion of the exponential terms produces a maximum error of no more than 10 per cent.

It will be noted that γ in general equation (4′) is, for cell no. 4 of type B represented by equation (17), more than 100 times the corresponding value for the class-A type represented by equation (15). The long time of sputtering produces a reduction of the metal-film resistance with increase in the thickness of the film; and if the light-transmission of the sputtered metal film in cell no. 4 were only approximately $\frac{1}{100}$ that of no. 5, γ would be increased accordingly. In that case, however, the selective absorption of the thicker film in cell no. 4 would give rise to a large change in spectro-photoelectric sensitivity; it will be seen later that the spectro-photoelectrical sensitivity curve for cell no. 4 is not very markedly different from that for cell no. 5. The increase in γ is therefore not solely due to increase in thickness of the metal film; from equation (14) it follows therefore that the increase in γ corresponds to a reduction in the value of R_c' for zero V'.

The B type of contact evidently yields a transition layer of a much smaller gap-width δ than the A type.

5·3. *Variation of short-circuit current with intensity of illumination.*

5·31. By measuring the p.d. across a number of standard resistances closing the

cell circuit in turn, the short-circuit current, corresponding to zero external resistance, can be found by extrapolation. Equation (11) shows that the relation between the short-circuit current and the intensity of illumination may be written

$$i_e = aE - bE^2 - cE^3 \qquad \text{.....(18),}$$

where a, b, c are constants.

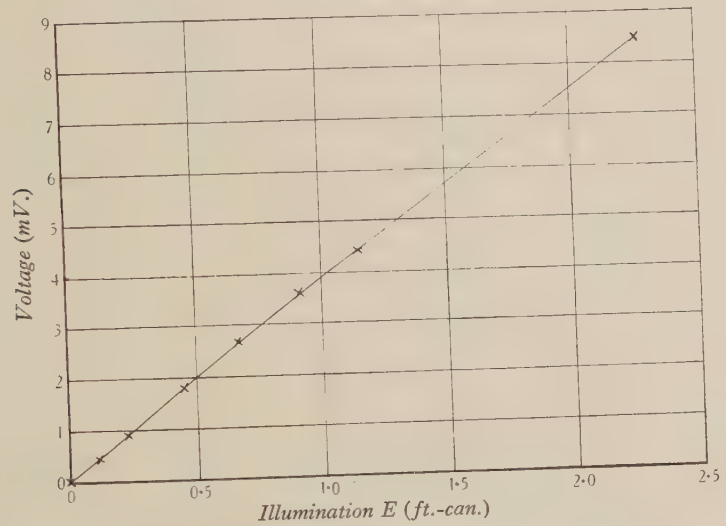

Figure 7. Curve for low illuminations, cell no. 6. Percentage transmission of neutral-tint filter = 1·012.

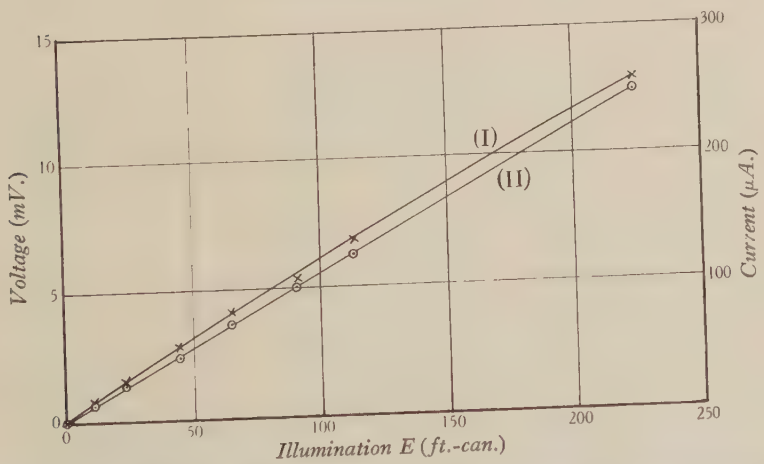

Figure 8. Curves showing illumination against (I) voltage and (II) current for cell no. 4

For the *A type of cell*, represented by no. 5, equation (18) applies over a range of values of E from 10 to 225 foot-candles to an accuracy of 4 per cent; when $a = 2$, $b = 1 \times 10^{-3}$, and $c = 2 \times 10^{-6}$, i_e is given in microamperes. It is evident that the range of measurement is too large for the assumption of a constant transmission coefficient, on which the above equation was based, to be precisely true. Over a

smaller range of E, such as 10 to 100 ft.-can., equation (18) can be taken as representing accurately enough the relation between i_e and E.

Further, in § 5·11 the assumption was made that Ohm's law holds for the resistances R_f, R_c and R_s. The validity of this assumption is confirmed by comparing the curves of short-circuit current against illumination for cells nos. 5 and 6,

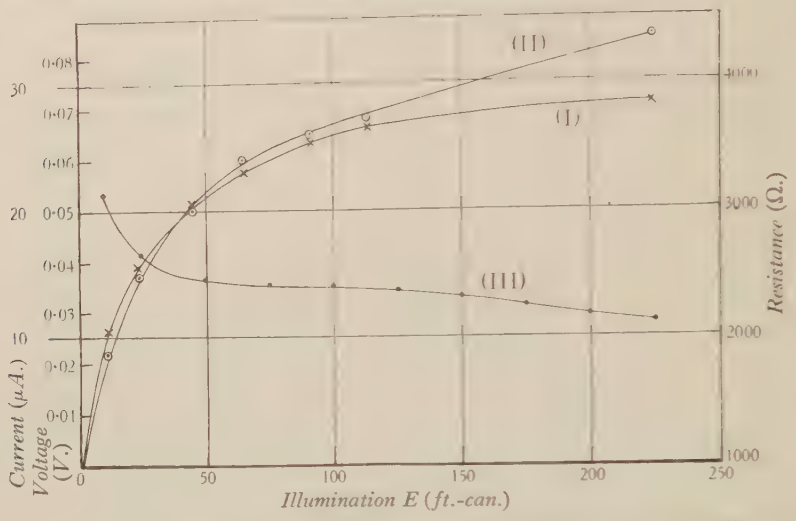

Figure 9. Curves showing (I) voltage, (II) current and (III) resistance against illumination.

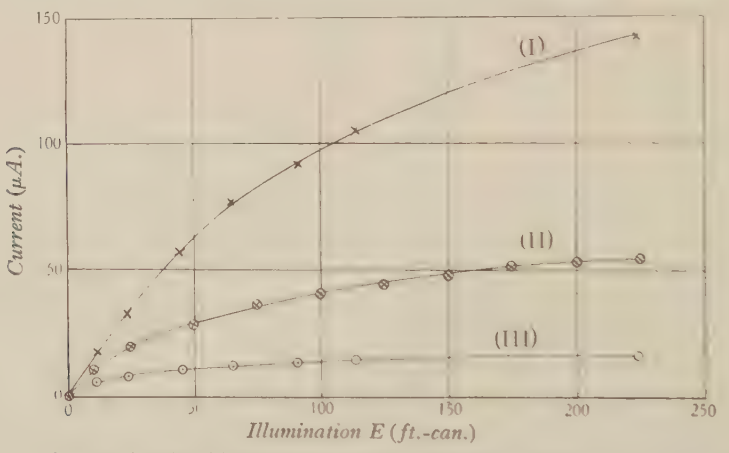

Figure 10. Curves showing illumination against current for various resistances in series with cell. (I) 1000 Ω.; (II) 2772 Ω., calculated current; (III) 10,000 Ω.

figures 3 and 6. Cell no. 6 is of A type, and only differs from cell no. 5 in having a thicker film of semiconductor, so that it gives rise to a larger value of R_s. For cell no. 5 when $R_c = 2772$ Ω., figure 10, the current-against-illumination curve is not very different from the short-circuit current-against-illumination curve for cell no. 6, figure 6. Thus in comparison with cell no. 5, no. 6 behaves as if it contained internally (in R_s) an extra fixed resistance of 2772 Ω.

For the B type of cell, represented by no. 4, figure 8, the coefficients b and c in equation (18) are so small that the deviation from true proportionality over the whole range 10 to 200 ft.-can. is negligible, i.e.

$$i_e \propto E \qquad \ldots\ldots(18').$$

5·32. If the constructional details relating to the types of cell represented by nos. 4 and 5 are varied, it is possible to construct cells whose response to illumination is very complicated. These cells can be of little practical use; figure 9, which gives the response curves for cell no. 7 (type B), is included to show the necessity for adhering to the constructional details specified in table 1.

5·4. *The cell resistance.* It is a common practice to term the quotient of the measured open-circuit voltage and the short-circuit current at a given illumination the "resistance" of the cell at that illumination. It must not be assumed, however, that at any given illumination the open-circuit voltage is equal to the short-circuit voltage across the transition layer. Let V' denote the open-circuit voltage, V_0 the short-circuit voltage (when $R_c = 0$), and i_e the short-circuit current at any given illumination E. Then

$$\frac{V'}{i_e} = (R_f + R_s)\frac{V'}{V_0} \qquad \ldots\ldots(19),$$

since $i_e (R_f + R_s) = V_0$. If therefore V'/V_0 is constant, V'/i_e is also constant. Experimentally it is always found that V'/i_e depends on E. From equation (19), therefore, the quotient V'/V_0 must depend on E, since R_f and R_s are to be considered as constant.

Experimentally, it has been found that for the A type of cell, represented by no. 5, the equation

$$\frac{V'}{i_e} = 6150 \exp(-14{\cdot}0V') \qquad \ldots\ldots(20)$$

holds over a range of E from 25 to 200 ft.-can.;

$$\therefore\ (R_f + R_s)\frac{V'}{V_0} = 6150 \exp(-14{\cdot}0V')$$

and

$$V_0 = \frac{R_f + R_s}{6150} V' \exp(-14{\cdot}0V') \qquad \ldots\ldots(21).$$

For the B type, represented by cell no. 4,

$$\frac{V'}{i_e} = 58{\cdot}1 \exp(-9{\cdot}0V') \qquad \ldots\ldots(22)$$

and

$$V_0 = \frac{R_f + R_s}{58{\cdot}1} V' \exp(-9{\cdot}0V') \qquad \ldots\ldots(23).$$

The quotient V'/i_e has been determined as a function of V' in order to give the relation between V' and V_0; V'/i_e is given in ohms and termed R in the figures.

It is seen from equation (18) that as E is decreased, i_e becomes more nearly proportional to E. When E is very small, i_e may with sufficient accuracy be taken equal to i_p. The value of the quotient V'/i_e then approaches R_c', equation (14), the contact resistance at zero voltage. Therefore, from equation (20) for cell no. 5, $R_c' = 6150\ \Omega$.; from equation (22) for cell no. 4, $R_c' = 58{\cdot}1\ \Omega$.

From equation (14) $\alpha \propto 1/R_c'$, and of course γ is directly proportional to α, so that $\gamma \propto 1/R_c'$. From equation (17) for cell no. 4, $\gamma = 399{\cdot}4$; and from equation (15) for cell no. 5, $\gamma = 3{\cdot}412$. The ratio of the γs for the two types is therefore 399·4 3·412 or 117·1; on the other hand, the ratio of the reciprocal of the corresponding contact resistances is 6150 58·1 or 105·9. The constant γ is also inversely proportional to the light-transmission of the metal film, and it follows therefore that the light-transmission of the metal film in cell no. 4 is approximately $90{\cdot}_5$ per cent that of the metal film in cell no. 5.

The quotient V''/i_c we interpret to represent the apparent variation of the contact resistance with V'' arising from the space-charge limitation of the current collected on open circuit by the circular electrode round the periphery of the metal film.

5·5. *Spectro-photoelectrical sensitivity.*

5·51. The spectro-photoelectrical sensitivity curves for unit incident energy for cells nos. 1, 4 and 5 are given in figure 11. The spectro-photoelectrical sensitivity for light of any given wave-length is defined as the current at that wave-length, relative to the current at the wave-length of maximum sensitivity, for the same amount of incident energy.

It is important to note how small are the differences between the three cells. This is at first sight surprising, since cell no. 1 was sputtered with gold for 23 minutes, no. 4 with silver for 60 minutes, and no. 5 with platinum for 4 minutes. A feasible explanation of the smallness of the differences is that the light-transmission of these metal films may be so high that they are not appreciably selective through the wave-length range 4000–8000 A.

5·52. Methods of measuring the thickness of these metal films were investigated with the object of determining whether the tentative explanation given in 5·51 could be supported experimentally. Unfortunately no direct measurements of their spectral absorption can be made. A metal film sputtered on glass would bear no relation, either with regard to the state of the deposit or the thickness of the film, to one deposited in the same time and under the same conditions on a semi-conductor surface. Thus it is necessary to seek an indirect method of determining the approximate thickness of these films.

Any experimental method not utilizing the film as deposited on the selenium-sulphur surface is open to objection. The method actually adopted and described below gives a maximum estimate of the average thickness. Two cells, nos. 9 and 10, were selected. J. J. Thomson[4] gives a formula for the resistance R of a circular lamina of thickness t so small that the currents are compelled to flow parallel to the
a, b lamina, being led in and out of the lamina by circular electrodes, radii a and b, placed on its circumference. This formula is

$$R = \frac{\sigma}{\pi t} \log_e \frac{r^2}{ab} \qquad \ldots\ldots(24),$$

r where r, assumed large compared with a or b, is the distance apart of the electrodes,
σ and σ the specific resistance of the lamina.

It was soon found that the surface conductivity of the selenium-sulphur could be neglected. Accordingly, the optically flat end-faces of two circular steel rods were pressed on to the circumference at the ends of a diameter of the circular metal

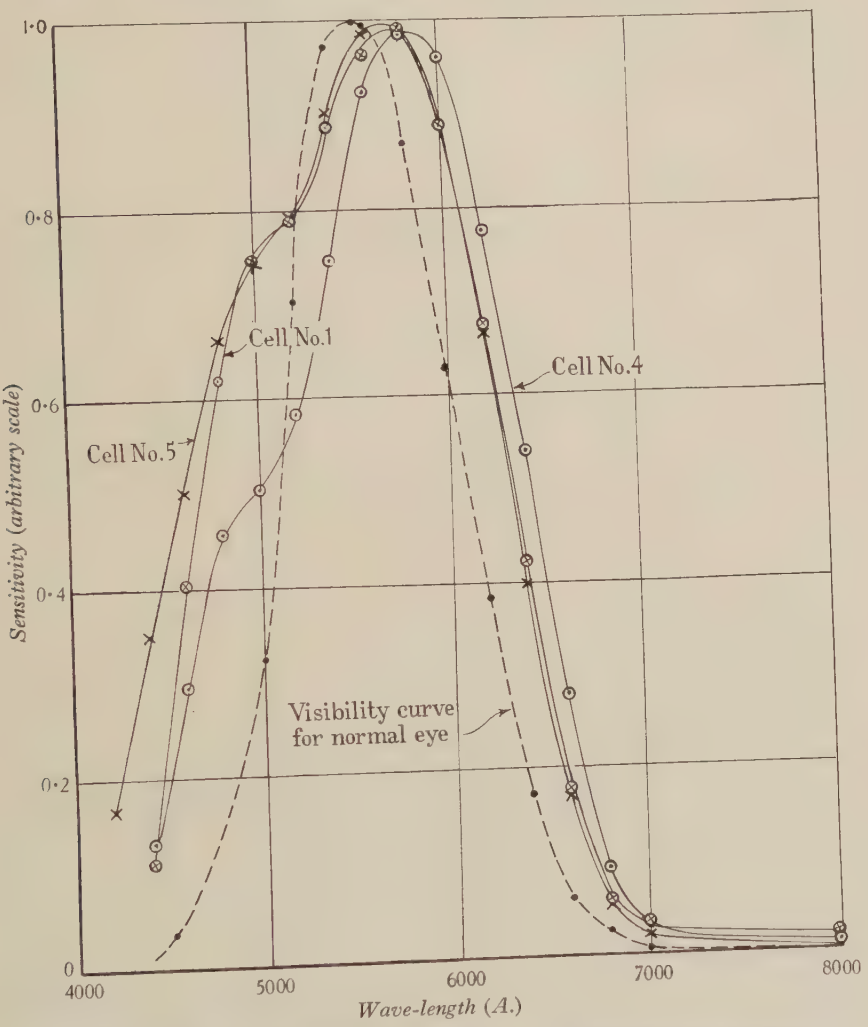

Figure 11. Spectro-photoelectrical sensitivity curves for unit incident energy: gold, silver and platinum films.

film. The current flowing when a voltage of 176·5 mV. was applied across the electrodes was measured. The resistances obtained were 400 Ω. for cell no. 9 and 290 Ω. for cell no. 10.

Now $\frac{1}{\pi}\log\frac{r^2}{ab}=1{\cdot}99$, so that equation (24) becomes

$$t=\frac{1{\cdot}99}{R}\sigma \qquad \text{.....(25).}$$

σ_p σ_g

For cell no. 9, $t = 4{\cdot}975 \times 10^{-3} \times \sigma_p$; for cell no. 10, $t = 6{\cdot}86 \times 10^{-3} \times \sigma_g$, where σ_p and σ_g are the specific resistances in very thin films of platinum and gold respectively.

An examination of published figures[5] for the specific resistances of thin metal films of gold and platinum was made, and those adopted for σ_p and σ_g are the highest possible values, viz. $\sigma_g \cong 50 \times 10^{-6}$, $\sigma_p \cong 150 \times 10^{-6}$.

With these assumed values, the *maximum* average thicknesses of the metal films in cells nos. 9 and 10 are $t \cong 7 \times 10^{-7}$ cm. for cell no. 9, and $t \cong 3 \times 10^{-7}$ cm. for cell no. 10.

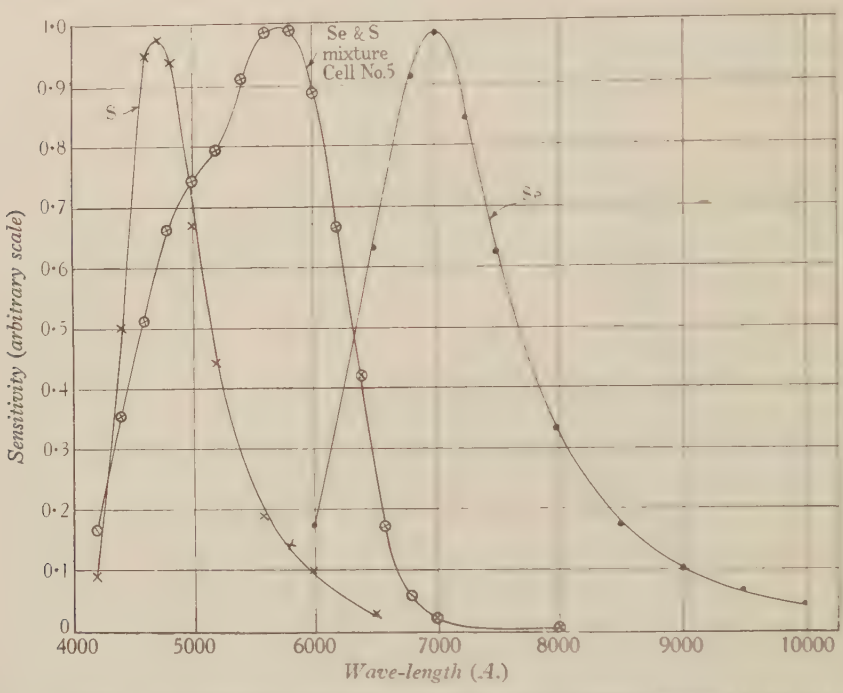

Figure 12. Spectro-photoelectrical sensitivity curves for unit incident energy: (*a*) for the primary photocurrent in sulphur; (*b*) in selenium; (*c*) for the contact photocurrent in rectifier cell.

Cell no. 1 was sputtered with gold for 23 minutes and no. 10 for 30 minutes; cell no. 5 was sputtered with platinum for 4 minutes and cell no. 9 for 15 minutes. The probable average thicknesses of the metal films in cells nos. 1 and 5 may therefore be assumed to be approximately between 1×10^{-7} cm. and 2×10^{-7} cm. Films of thickness 10^{-7} cm. deposited on glass show a variation of only a few per cent in spectral transmission throughout the range 4200 8000 A., and the mean transmission is of the order of 90 per cent according to the International Critical Tables. The thickness of the film in cell no. 4, sputtered with silver for 60 minutes, is greater (see § 5·4) than that of the films in cells no. 5 and no. 1; but it must still be less than 10^{-6} cm. for the explanation given in 5·51 for the smallness of the differences between the spectro-photoelectrical sensitivity curves in figure 11 to hold.

5·53. In figure 12, the spectro-photoelectrical sensitivity for the internal primary photocurrents in selenium and in sulphur (obtained from Gudden's curves[6] and

Kurrelmeyer's curves[7] respectively) is plotted in addition to the spectro-photoelectrical sensitivity for cell no. 5. It is seen from the curves that the threshold energy for the contact photocurrent appears to be greater than for the internal primary photocurrent. Frenkel observed this to be true of the cuprous-oxide rectifier photoelectric cell also, but inferred from his theory that the contact effect actually began at the same frequency as the internal effect, and only became appreciable at a certain higher frequency which decreased as the width of the contact gap increased. The small but marked displacement towards the longer wave-lengths of the curve for cell no. 4 in figure 11 as compared with that for cell no. 5 cannot therefore be due, if Frenkel's theory is correct, to the known differences in the widths of the contact gaps; it can, however, be reasonably ascribed to absorption by the silver film.

5·54. In the selenium photoconducting cell the number of electrons which must be set free in order to account for the increased conductance of selenium under a given illumination far exceeds the number which could be set free by photoelectric action of the absorbed light according to the quantum equivalence principle. The theories of the light-sensitivity of the selenium photoconducting cell remained obscure and doubtful, until Gudden and Pohl[6] succeeded in accounting for the observed changes in conductance by observations of the secondary effects following primary ionization; they proved that secondary photocurrents arise which are essentially electrolytic in nature.

In the rectifier cells dealt with in this paper the current produced can be associated directly with the primary photoelectrons, as in the case of the photoemissive photoelectric cell.[8] Qualitatively all that is necessary is to show that the maximum measured current for any given incident flux is appreciably smaller than the maximum theoretical photoelectric yield. Accordingly if each point on the spectral-energy distribution curve[9] of the tungsten-filament source is weighted according to the spectro-photoelectrical sensitivity of cell no. 5, integration of the resultant curve will give the total effective energy-emission of the lamp. Thus from the known area of the cell the effective incident energy can be calculated for an illumination of 200 ft.-can. If this energy were concentrated in a narrow band of wave-lengths in the region of maximum sensitivity (5700 A.) and completely converted, the electrical yield according to the quantum equivalence principle would be of the order of 6500×10^{-6} A. For cell no. 5, the current obtained at 200 ft.-can. is only 343×10^{-6} A. It is therefore reasonable to conclude that the observed photocurrent is directly associated with the primary photocurrent arising from the optical release of bound electrons. The assumption has already been stated in the discussion of theories in § 2.

If the current density in R_s is very high, one must expect the cell to show all the known characteristics of selenium resistances, namely drifting, inertia and remanence effects, and such have been observed with high values of the incident illumination. For accurate work, therefore, it is important to restrict the use of the cells here described to illuminations giving a short-circuit current not exceeding 100 μA.

§ 6. SEALING OF CELLS

Absorption of moisture is found to lead to disintegration of the sputtered film and to complicated behaviour of the selenium resistance R_s. Work is in progress on the use of moisture-proof colourless lacquers. The results given in this paper were obtained as soon as possible after construction of the cells, which were kept in a desiccator over phosphorus pentoxide.

§ 7. ACKNOWLEDGMENTS

The author is indebted to Mr L. H. McDermott, B.Sc., A.R.C.S., D.I.C. for his assistance in the determination of the spectro-photoelectrical sensitivity, to Mr C. J. W. Grieveson, B.Sc., M.A. for his assistance in the experiments with the iris diaphragm, and to Mr W. A. Wood, M.Sc. and Dr G. Shearer of the Physics Department for the X-ray examination of the selenium-sulphur mixture. He also wishes to record his sincere thanks for the kind interest and encouragement of Dr J. W. T. Walsh and of Mr J. S. Preston, M.A., F.Inst.P. and particularly for much valuable criticism by Dr D. Owen.

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DISCUSSION

Dr Walsh. The type of cell which the author has studied is of great and continually increasing importance to those who are interested in the measurement of illumination and in photometry generally. It is therefore of great value to have a description of the way in which these cells can be made, so that the mystery which has hitherto surrounded their construction no longer daunts anyone wishing to adapt them to a particular problem or type of measurement.

For illumination photometry the two matters of outstanding importance are (i) the spectral sensitivity curve, and (ii) the extent to which the sensitivity of the cell varies with the obliquity of the incident light. The ideal would be a cell which was unaffected by obliquity and for which the sensitivity curve was exactly the same as that for the eye. It is greatly to be hoped that the author will continue his researches and so bring this ideal nearer to realization than it is at present.

Dr M. Benjamin. There are one or two points in the paper on which I am not quite clear. How exactly is the current carried through the selenium-sulphur film? Is it electronic or electrolytic in nature? The theoretical treatment in the paper makes use of Wilson's theory of semi-electronic conductors. This theory depends on the presence of an impurity in the pure substance, the impurity atoms supplying electrons to the empty energy-band of the pure substance, these electrons then becoming conduction electrons. If the theory is applicable to these rectifying cells, it would appear that the current should mainly be conducted electronically.

The author states that spectroscopic evidence indicates that the amount of any impurity is probably insufficient to allow Wilson's theory to apply. Actually the theory will apply even when the impurity-concentration is only of the order of one part in one million. Does the author believe that the conductivity is at all dependent on the presence of a suitable impurity, and if so, has he any views as to its nature? With regard to the marked dependence of the conductivity on the annealing temperature of the sulphur-selenium film, may it not be that the exact nature of the sulphur-selenium lattice is dependent on the annealing temperature? Alterations in the lattice will result in alterations in the energy levels, and therefore in the conductivity.

The X-ray examinations showed that mixed crystals of selenium and sulphur were formed. Did the chemical composition agree exactly with the amount of sulphur added, or is the composition dependent on the annealing temperature? If the solid solution does vary in composition, this may explain the variations in conductivity.

Author's reply: I should like to thank Dr Walsh for his comments on my work. Dr Benjamin's first question concerning the nature of the electrical conduction in the selenium-sulphur film is answered in paragraph 5·54. Owing to the extreme difficulty of determining both the nature and the amount of the impurities present in the elements used for these cells, any discussion as to how the conduction electrons are derived can have little scientific value. Undoubtedly, the formation of the selenium-sulphur lattice is greatly influenced by the annealing temperature. This has been studied in the case of selenium alone, and the results are considered in my book *The Selenium Cell*. The formation of the eutectic mixture of the selenium and sulphur depends, of course, upon the annealing temperature.

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THE DEVELOPMENT OF THE PHOTOGRAPHIC LENS

By W. TAYLOR and H. W. LEE, Research Department, Taylor, Taylor and Hobson, Ltd., Leicester

Address delivered on January 18, 1935.

§ 1. INTRODUCTION

This address has been prepared with two main objects. The first is to give British physicists a better conceit of their national heritage, based on the knowledge that the principal fundamental inventions concerned in the development of photographic lenses have been British inventions. The second is to show that, with one exception, the development of photographic lens design has consisted at each successive step of only a small advance on traditional design.

This process of development, which is usual with inventions in general, is well illustrated by the case of the shot gun in its descent from the bow and cross-bow. When gun-powder was invented the cross-bow was in use, and the barrel of the shot gun was fastened to the old stock of the cross-bow; but because it was not seen how to use the trigger, this remained for a time out of use, like the buttons on the back of our tail coats. A touch-hole was put in the side of the barrel so that the charge could be exploded by a match applied to the mouth of the hole. Then, the better to ensure ignition, the mouth was enlarged into a pan which had to be separately primed, and presently a hinged cover was fitted to keep the priming dry. Gradually the trigger came into use again; a spring-urged cock was fitted to carry a flint, and the trigger held this ready for action. When the trigger was released, the flint came down, lifted the cover from the pan, and struck a spark which ignited the priming.

In the course of time the percussion cap was invented, the flint was discarded and the cock became a hammer to strike the separate percussion cap. Then the charge of gunpowder was put in a packet for better convenience and to save time in loading the gun, but the packet had to be broken to expose the powder. This was the beginning of the cartridge. Presently it was seen that it would be better to attach the percussion cap to the cartridge, and in order to reach the cap each cartridge was provided with a pin projecting from its side ready to be struck by the hammer in the gun; but the gun had to be altered to receive this cartridge and became a breech loader. The cartridges were dangerous things to carry, and had to be placed in the gun in a particular way with the pin toward the hammer, and in time the pin was put in the axis of the cartridge. Afterwards it was seen that it was superfluous and dangerous to provide each cartridge with a pin, so the pin was housed once for

all in the gun and the percussion cap set flush in the head of the cartridge as we now know it; but for a long time the hammer of the gun operated transversely to the axis of the gun, and finally it was changed to operate along the axis in line with the pin.

The development of the photographic lens has followed a similar course and with few exceptions has clung closely to tradition.

§ 2. FORM OF SURFACE

The ordinary photographic lens has hitherto employed spherical surfaces, mainly for the reason that no other form of surface has been commercially attainable with the requisite accuracy. The order of accuracy commonly desirable and commonly attained is within one or two wave-lengths of light, measured as departure from sphericity by means of an accurate counterpart of the surface placed in contact with it so as to exhibit any disconformity by means of Newton's rings. Lens-surfaces of such accuracy are, and probably must always be, produced by grinding and polishing with abrasive charged laps; and the only form of tool which can be moved upon the work in various directions to abrade it while maintaining continuous surface contact with it so as to govern its shape is the spherical form.

No appliances based upon mere line or point contact have hitherto been made, nor probably ever will be made, sufficiently rigid to operate commercially with this accuracy.

§ 3. HISTORICAL

The first step. The use of simple lenses with spherical surfaces for forming images of objects goes back to antiquity. It was Chester Moore-Hall an English amateur who in 1733 discovered, and Dollond an English optician who in 1757 independently re-discovered and "reduced to practice", the fact that by suitably combining a double-convex collective lens of crown glass with a nearly plano-concave dispersive lens of flint glass, it was possible to correct the chromatic error of single lenses which causes different colours of the spectrum to focus at different distances. They also discovered that, by the same means, it was possible to correct the so-called spherical aberration of the single lens which causes rays of light from one object point, incident at various zones of the lens surface, to focus at a corresponding variety of distances instead of at one common distance. The angular extent of the image well defined by Dollond's objective was only about one or two degrees, but this invention furnished the common form of telescope objective used for over a century, and still used; and this became the nucleus from which more and more perfect lens systems for photography were evolved.

The second step in this evolution was made in 1830 by Lister, the father of Lord Lister, who constructed microscope objectives by combining two of Dollond's telescope doublets (the two flints facing the object which he wished to magnify) to obtain increased aperture and illumination, and he so spaced them apart that they corrected each other's coma.

The third step was collateral with Dollond's invention. In 1802 Wollaston, an English physician and amateur optician, discovered how to correct astigmatism and produce lenses giving reasonably well-defined images of greater angular extent. He applied his invention first to the correction of the astigmatism of spectacle lenses, and in 1912 to the camera obscura and camera lucida. He perceived that in order to be free from astigmatism the lens must focus at the same distance lines radial in the field and lines at right angles thereto; and this he secured, as shown in figure 1, by giving the lens a meniscus form and placing a stop at a suitable distance from its concave side. The significance of the distance was that it determined the particular zone of the meniscus through which light passed at any given angle to the lens axis. Probably Wollaston arrived at his discovery experimentally, but it readily follows from consideration of the first-order aberrations.

I, d If E is the coefficient of spherical aberration, I that of coma, and d the distance of the stop from the lens, the condition for removal of astigmatism in a simple lens with a stop is

$$Ed^2+2Id+1=0 \qquad \text{.....(1).}$$

For a collective lens, E is positive and d^2 necessarily so; so that Id must be negative, i.e. the coma will be of different sign according to whether the stop is placed in front of or behind the lens. In the case of spectacles the stop or diaphragm is the centre of rotation of the eye, and is consequently on that side of the lens remote from the object. A century elapsed before the advantages of Wollaston's meniscus spectacle lenses were generally appreciated, but the form is now in common use.

In the camera obscura Wollaston placed the lens between the stop and the focal plane or, as we should say, placed the lens behind the stop, so that d is positive in equation (1); consequently I must be negative. It can easily be shown that equation (1) always yields two real solutions if the lens is a meniscus with its concave surface facing the stop. Of course, in practice the smaller value of the stop-distance d is used.

If the lens is placed in front of the diaphragm, d is negative and I must be positive. It can be shown, by putting in the value of the aberrations in terms of the lens form, that there will be real roots only if the ratio of the power of the first surface to that of the lens is greater than the square of the refractive index. This relation seems to have been overlooked for a century, and from it a construction of meniscus lens has recently been patented[1].

The locus of all image points in the field of Wollaston's lens (which he called periscopic) was not a plane but a surface concave to the lens—in current terms, his lens had an uncorrected field; also it was not corrected for spherical or chromatic aberration or distortion. At small apertures, however, the definition was sufficiently good for early photographic cameras and this simple meniscus of Wollaston is still made by the million for cheap cameras.

h Of *the fourth step*, the correction of distortion, the authorship is disputed, but it is based on Wollaston's invention and dates from about 1860. Distortion h can be expressed in terms of the other aberrations by an equation which, for a simple lens, has the form:

$$h=(3+1/n)\,d+3I.d^2+E.d^3 \qquad \text{.....(2)}$$

and this cannot be zero unless $d=0$. It follows from the equation that if two lenses are equally spaced on opposite sides of a stop, and have equal powers F and equal amounts of coma but of opposite signs, the distortion will be small if E, the coefficient of spherical aberration, is not large, since E is multiplied by the cube of a small quantity d. These conditions are nearly satisfied by employing two equal menisci on opposite sides of a diaphragm. Such a system is also approximately free from coma. It is still used in photography, generally under the name of "the periscopic system". The aberrations still uncorrected are spherical and chromatic aberrations and field curvature, and these limit the aperture to about $f/11$.

The next problem to arise was that of increasing the aperture of the lens in order to make portrait photography commercially feasible. This, *the fifth step*, was first taken by Joseph Petzval, a Hungarian mathematician, in about 1840. His lens in shown in figure 2. Starting with the objective of Dollond, corrected for spherical

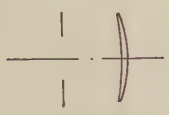

Figure 1. Wollaston's meniscus lens, 1812.

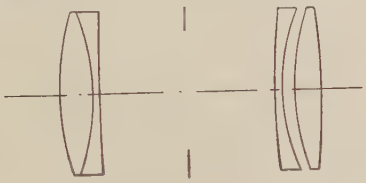

Figure 2. Voigtländer (Petzval) portrait lens, 1840.

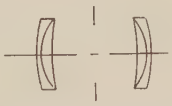

Figure 3. Dallmeyer rapid rectilinear, British patent specification no. 2502/1866. A. Steinheil aplanat, Bavarian Pat. 1866.

and *chromatic* aberrations, he placed a stop behind to correct its astigmatism as Wollaston had done. He chose a form with rather a small value of coma, but this entails a large stop-distance, as equation (1) shows. Behind the stop he placed another pair of lenses and at such a distance that their astigmatism was corrected by the stop. These pairs of lenses were *separately corrected* for spherical and chromatic aberrations and the rear pair had coma equal but of opposite sign to that of the front pair (whence the difference in form), so that the comas cancelled out. His complete system was thus corrected for spherical and chromatic aberrations, coma and astigmatism, and he realized an aperture of $f/3$ (i.e. the diameter was one-third of the focal length).

Petzval's lens had the disadvantage that curvature of field was uncorrected and further that, owing to the great distance of its members from the stop and from one another, its field was very small (with a total angle of about 15°). Nevertheless, in the hands of the portrait photographer (a great conservative) this lens largely survives.

In the 'sixties Dallmeyer in England and Steinheil in Germany, concurrently, took *the sixth step* by introducing the rapid rectilinear lens which gave the photographer a lens with a moderately extended field. The rapid rectilinear (or rapid symmetrical or rapid aplanat, as it was variously called) is shown in figure 3. It also started from the inventions of Dollond and Wollaston, and employed two cemented *achromatic* doublet objectives, each with a large amount of coma and consequently requiring only a small stop-distance to correct the astigmatism, equation (1). The two faced one another so that one was the mirror of the other with respect to the

stop, and thereby coma and distortion were corrected, see equation (2)—hence the name "rectilinear". The large amount of coma was obtained through suitable choice of glass. If cemented achromatic doublets free from spherical aberrations are calculated for a number of different pairs of glass (crown and flint), it will be found that those made from pairs having small differences in refractive index and in dispersion have larger amounts of coma than those made from pairs having greater difference in these optical properties.*

The inventors of the rectilinear lens employed light flint glass for the crown lens, together with the usual dense flint. The smallness of the difference in refraction and dispersion between these two glasses produced a doublet having a large amount of coma, and of meniscus shape with very deep curves. The small stop-distance determined by the coma made the system short, and the lens had the comparatively large field of 40° to 50°, but the depth of the curves limited the aperture to *f* 8, and it could not have freedom from astigmatism and a flat field at the same time.

In 1827 G. B. Airy, Astronomer-Royal, indicated the requirements of the next, *the seventh step*, the flattening of the field. He pointed out that the locus of the focus of points off the axis was different when the rays are in the plane containing the object point and lens-axis (primary plane) from the locus when the rays are in a plane perpendicular thereto (secondary plane). The two loci he found for a single lens (considering up to the second power of the angle of field) to be circles both concave to the lens and having the respective radii of curvature $nf(3n+1)$ and $nf/(n+1)$, where f is the focal length and n the refractive index. If astigmatism is corrected the two loci coincide with a radius of field curvature of nf. Airy's work was unknown on the continent and thirteen years after his publication (in 1840) the condition for flatness of field was independently discovered by J. Petzval.

Instead of considering the radii of curvature as Airy did, it is usual to consider the curvature of the field, viz. $1/nf$ for F/n, where F is the power of the lens. Then for a system of thin lenses the total curvature of the field is the sum of the values F/n. In particular for a pair of glasses, as in an achromatic doublet, if F_1 and F_2 are the respective powers and the glass materials are defined as n_1 and v_1 and n_2 and v_2 respectively, the condition for flat field is:

$$F_1/n_1 - F_2/n_2 = 0,$$

and the condition for achromatism is:

$$F_1/V_1 - F_2/V_2 = 0,$$

V is defined as $(n-1)/(n_1-n_2)$, where n_1 and n_2 are the refractive indices for the two rays to be achromatized, and n their mean value.

If these two equations are to be consistent, a large refractive index must be associated with a large value of V or a small dispersion, and glass of low index should have large dispersion, whereas in the crown and flint glasses alone available in the time of Airy and Petzval high index was associated with high dispersion.

In 1888, Abbe and Schott produced glasses with the necessary properties, and

* This has been discussed for example in *Constructional Data of Small Telescope Objectives*, by T. Smith and R. W. Cheshire.

soon afterwards Schroeder (of Ross) patented[2] the first anastigmat, that is, a lens having a substantially flat field substantially free from astigmatism. The lens, which is shown in figure 4, consisted of two *achromatic* doublets each using the new barium crown glass of high refractive index for the outer glasses, and the new light flint glass of low refractive index for the inner glasses to correct the field; astigmatism and coma were corrected as in Wollaston's invention by suitably spacing the stop in relation to the lens members. Correction of spherical aberration was impossible with this form of lens, as it would require the refractive index of the flint to be higher than that of the crown. The aperture was accordingly limited to $f/16$.

Thus it seemed that the new glasses had removed one aberration, field-curvature, at the expense of another, spherical aberration. Rudolph (of Zeiss) then conceived the idea, shown in figure 5, of combining an *achromatic* doublet in front made of old glasses, which would correct the spherical aberration, with one in the rear made of the new glasses, to flatten the field. This in 1890[3] was the first anastigmat cor-

Figure 4. Ross (Schroeder) concentric, British patent specification no. 5194/88.

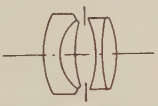

Figure 5. Zeiss (Rudolph) protar, British patent specification no. 6028/90.

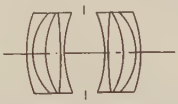

Figure 6. Zeiss (Rudolph) double protar, British patent specification no. 19,509/94.

Figure 7. Goerz (v. Hoegh) dagor, British patent specification no. 23,378/92.

Figure 8. Zeiss (Rudolph), British patent specification no. 4692/93.

rected for spherical aberration. The old achromat was in front and the new achromat behind the diaphragm. The aperture was $f/7{\cdot}5$, and slightly better than that of the rectilinear lens. Four years later[4] he combined his old and new achromats in one, making a quadruplet which he duplicated. This is shown in figure 6.

The order of refractive indices in each member was: low-index flint, high-index crown (forming the new achromat), low-index crown, high-index flint (forming the old achromat). Two of these quadruplets were used, one before and one after the diaphragm, to correct coma and distortion. The new achromats were the inside pairs and the old the outside pairs of the complete system of eight glasses.

Von Hoegh (of Goerz) in 1892[5] accomplished the same result with only six elements, figure 7. He placed the pairs of new glasses outside instead of inside the pairs of old glasses so that the order of refractive indices was such that in each half of the system he could give two interior elements the same index, and these became one single double-concave dispersive element, which was set between two collective elements. Zeiss afterwards adopted the same simplification with a similar sequence of refractive index, figure 8. His components consisted each of a double-convex element between a double-concave element next the stop, and a meniscus dispersive element outside. But this form was abandoned by Zeiss in favour of the earlier eight-element type.

§4. THE BREAK FROM TRADITION

We have seen that up to this time the practical development of the photographic lens had proceeded step-by-step along lines which had become traditional and which tended to more and more elaborate constructions. In the earlier stages Englishmen had taken a predominant part, not only in invention but in the mathematical treatment of the subject. Airy's work was extended in 1829 and 1830 by the Cambridge mathematician Coddington, whose work was in turn the basis of Dennis Taylor's and was developed by him in his *Applied Optics* published in 1906; but latterly the Germans had taken the lead, and this was due partly to the theoretical work of Von Seidel who had, in 1856, reduced the mathematical expressions for optical aberrations to forms more convenient for the use of lens-computers than any previously published in the German language, and partly to the stimulus given by the glass production of Abbe and Schott.

In 1893 another Englishman, with the penetrating vision of genius and the true spirit of inventiveness, stepped aside from tradition and solved this complex problem by using only three lens elements. This was H. Dennis Taylor who was

Figure 9. Taylor-Hobson (H. D. Taylor) Cooke lens (final form), British patent specification no. 15,107/95.

Figure 10. Dallmeyer (Aldis) stigmatic, British patent specification no. 16,640/95.

honoured for his work by receiving the Duddell Medal of this Society last year. He satisfied the Airy-Petzval condition in a new way; see figure 9. He began by considering a collective and a dispersive lens of equal or approximately equal power, and spaced apart so that they had a combined collective power to form a real image. If two lenses of powers F_1 and F_2 are separated, and the weaker (if they are not equal) is dispersive, then the system is collective and the greater the separation the greater the power; but the Airy-Petzval sum, indicating the degree of curvature of the field, remains the same whatever the separation. Consequently, by employing a negative and a positive lens separated from one another, it is possible to correct the curvature of field with almost unlimited choice of refractive indices.

In order to correct distortion he divided the postulated collective component into two, placing one part on one side of the dispersive component and the other on the other side. Hitherto it had been considered necessary to achromatize each separate component of a lens system in order to achromatize for points off the axis. Dennis Taylor, although in his first design he followed this tradition, subsequently discovered that he could achromatize the system as a whole without achromatizing the individual components. He corrected spherical aberration and coma by suitable choice of curves, and astigmatism by making the separation from the stop of the collective components greater than that of the dispersive component, i.e. he placed the collective elements outside the dispersive element, and the stop near to the last.

No fundamentally new principle of photographic lens design has been originated since Dennis Taylor invented this lens forty years ago.

H. L. Aldis (then with Dallmeyer), in his "stigmatic" lens, figure 10[6], changed the order of Dennis Taylor's elements by placing the dispersive outside the collective components. This necessitated, in all components, a meniscus form for the correction of spherical aberration and the compounding of some or all of them for chromatic correction.

§ 5. INFLUENCE OF THE CINEMA

During the latter half of this period the predominant influence in the development of photographic lenses has been that of the cinema and film production; and this has demanded lenses substantially free from all aberrations and of increasingly large apertures.

At first when lenses with apertures so large as $f/2$ were offered to the photographers in Hollywood they were rejected because experience had taught that apertures must be limited in order to get sufficient depth of focus; but this objection has been removed by the realization that for a given size of final image the shorter the focal length of the lens used for the original photograph the greater is its effective depth of field, and owing to the small area of the cine film picture (the "frame") relatively short-focus lenses with larger apertures have come into use. Thus the glare and heat of excessive illumination are reduced, greatly to the comfort of the actors.

The recent development of fine-grain photographic emulsion for cinema film has stimulated a general demand for smaller cameras and lenses of proportionately short focal length, greater consequent depth of field, greater rapidity, and generally more critical definition.

In these and other developments, since the date of Dennis Taylor's invention, three principal types or families of lens have been the subjects of work by various opticians. First the continental type of lens based on the designs of Rudolph (of Zeiss), figure 6, and Von Hoegh (of Goerz), figure 7, which are capable of yielding relatively large field but with restricted aperture. Second, the Petzval type, figure 2, characterized by extreme aperture but small field; and third, lenses based on the principles of Dennis Taylor's invention and characterized as being capable of yielding both extreme aperture and moderately large field.

§ 6. THE CONTINENTAL TYPE OF LENS

Lenses of the continental type had one advantage in the eyes of photographers, namely their convertibility. Since they were made of two similar components of different focal length, separately achromatized, either component could be used by itself as a partially corrected lens and with these the photographer had two, or sometimes three, different lenses at his disposal. Continental design was directed either to improving the performance of the separate half-lenses or to increasing the aperture, both aims generally leading to greater complexity of design. Messrs Watson increased the aperture of the Zeiss six-lens $f/6{\cdot}8$ convertible lens to $f/4{\cdot}8$, while Messrs Ross (Mr Hasselkus) increased the aperture $f/6{\cdot}8$ of the Zeiss eight-lens formula to $f/5{\cdot}5$ in their "combinable" lens[7], while Taylor, Taylor and

Hobson (Mr Lee)[8] further extended the aperture to *f* 4·5. Ross (Hasselkus and Richmond) increased the aperture, *f* 6·8, of the Goerz lens to *f* 4 by separating one element in each component, figure 11[9]. This lens, on account of its large field (70°) and aperture, has proved valuable for photographic aerial survey work. Other modifications were made by Steinheil and Voigtländer, figure 12.

The greater complexity resulting from efforts directed to increasing the convertibility of this type of lens is shown in lenses made by Goerz, figure 13[10], Turner and Reich[11] and Taylor-Hobson (H. W. Lee), figure 14[12].

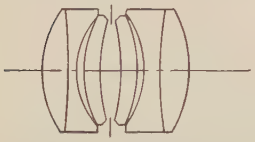

Figure 11. Ross (Hasselkus and Richmond) wide angle, *f*/4, British patent specification no. 295,519.

Figure 12. R. Steinheil orthostigmat, British patent specification no. 12,949/95. R. von Voigtländer collinear, British patent specification no. 18,723/96.

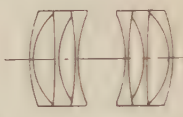

Figure 13. Goerz (v. Hoegh), British patent specification no. 13,904/97.

Figure 14. Taylor-Hobson (H. W. Lee) convertible, British patent specification no. 376,044.

§7. THE PETZVAL TYPE OF LENS

To supply the demand for more rapid lenses the Petzval type of lens has been developed, and Mr Warmisham (of Taylor, Taylor and Hobson) has invented many modifications and improvements of this lens, taking the aperture to *f* 1·5. The form illustrated in figure 15 has proved particularly suitable for use in the photographic recording of sound, on account of its field correction. Figure 16 shows a modified Petzval lens by Kodak. Zeiss, by adding another element, figure 17, have recently

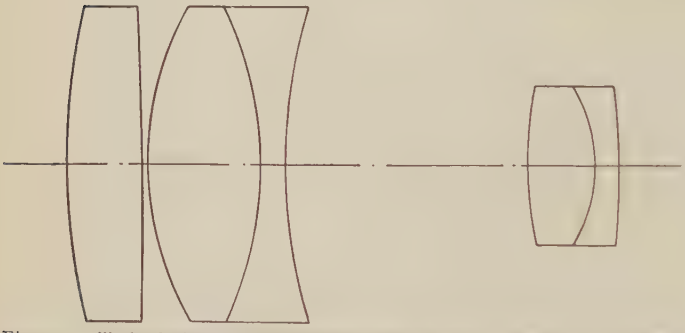

Figure 15. Taylor-Hobson (A. Warmisham), British patent specification no. 342,889.

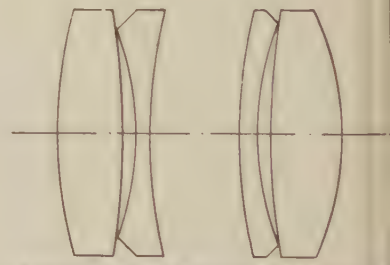

Figure 16. Kodak (Frederick and Altmann), U.S. patent specification no. 1,620,337.

extended the aperture to *f* 0·85 to make possible the cinematography of X-ray skiagrams, work specially associated with the names of Drs Russell Reynolds in England and Robert Janker of Bonn. These high-speed lenses retain the characteristic qualities of the original Petzval lens, namely narrow angle of field and field curvature, faults which become aggravated as the aperture is increased.

§ 8. DESCENDANTS OF THE H. D. TAYLOR TYPE OF LENS

With the continental type of lens restricted in its aperture, and the Petzval type in its field, the invention of Dennis Taylor has become more and more dominant and the subject of development by various opticians.

Dennis Taylor's lens of three simple elements can, by the use of glasses made available since the date of his invention, be made capable of performance over a field of 40° at an aperture of $f/3$ or, in the case of short-focus lenses, an aperture of $f/2{\cdot}5$.

He had shown that while only two lenses, collective and dispersive, were necessary for field-flattening, it was necessary to divide the collective lens into two for the sake of other aberrations. He also suggested that the dispersive lens could be divided into two, and these elements could be placed one on each side of the stop and between the two collective lenses as shown in figure 28. These two forms of Dennis Taylor's invention, which may be called the "triplet" and the "quadruplet", have been the parents of later developments which have generally consisted in (*a*) replacing one or more of the simple elements by more or less complicated cemented components; (*b*) replacing one or more single elements by a pair or pairs of elements of like kind (for example as the quadruplet arose from the triplet), and (*c*) combinations of (*a*) and (*b*).

Many of these modifications have resulted in improved performance of the type, and some of them have resulted in avoiding patent claims! Before illustrating examples of these elaborations of the original Dennis Taylor lens, we illustrate, in figure 18, a modification due to H. L. Aldis in the cementing together of the front pair of elements. We have selected for illustration a number of characteristic developments of the Dennis Taylor triplet.

In the class (*a*) may be mentioned the Zeiss tessar (Rudolph and Wandersleb), figure 19, in which the back component is double though not achromatized, and the Voigtländer heliar, figure 20, in which both front and back are made double. L. B. Booth also compounded the front and back to produce the Dallmeyer $f/2{\cdot}9$ lens, figure 21.

Recent developments, figure 22, of the triplet are due to Berek (of Leitz)[13] who, by making all the components complex, realized an aperture of $f/2$; and, figure 23[14], apertures $f/2{\cdot}8$ to $f/2$, to Zeiss.

In the second class (*b*) comes the Taylor-Hobson $f/2{\cdot}5$ lens, figure 24, with double-back component, and the Ernemann (now Zeiss-ikon) series of lenses having apertures up to $f/2$, figure 25, in which the front lens was first divided into two separate simple elements but is now compounded, though not achromatized, and falls into class (*c*), figure 26. Figure 27 shows an example of divided dispersive component, the Meyer plasmat $f/1{\cdot}5$. The most useful form of this class (*b*) is that in which both dispersives are double-concave, in accordance with the original suggestion of Dennis Taylor. This quadruplet was developed by Goerz in their celor and dogmar lenses, and further, figure 28, by Warmisham (Taylor, Taylor and Hobson) for photography from aircraft during the war[15], for which purpose he improved its corrections for oblique spherical aberration and coma and for zonal astigmatism, so

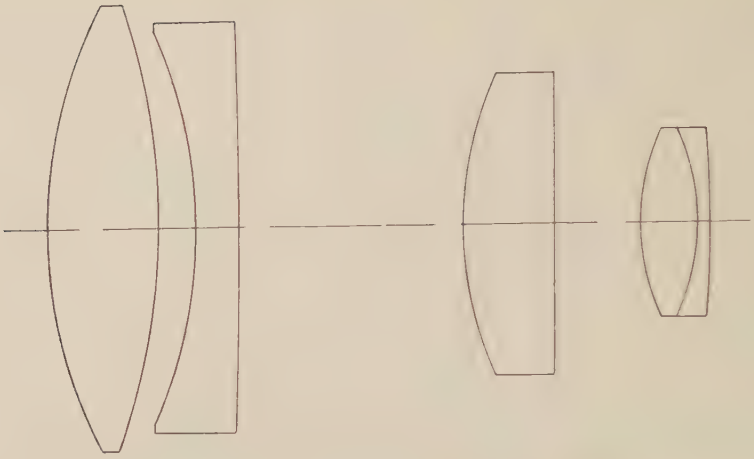

Figure 17. Zeiss *F*/O 85, U.S. patent specification no. 1,967,836.

Figure 18. H. L. Aldis, British patent specification no. 5170/01.

Figure 19. Zeiss (Rudolph and Wandersleb) tessar, British patent specification no. 13,061/02.

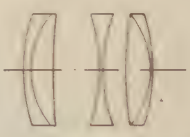

Figure 20. Voigtländer (Harting) hilia, British patent specification no. 13,441/02.

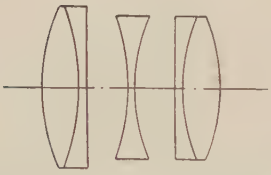

Figure 21. Dallmeyer (L. B. Booth) pentac, British patent specification no. 151,506.

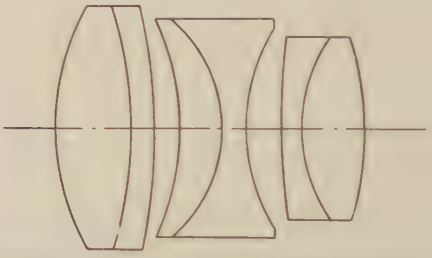

Figure 22. Leitz (Berek), British patent specification no. 382,246.

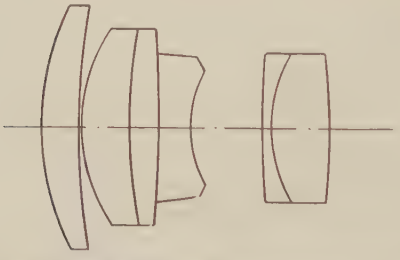

Figure 23. Zeiss, British patent specification no. 383,591.

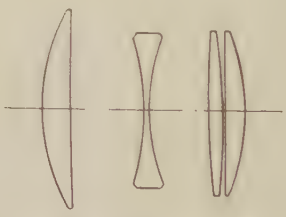

Figure 24. Taylor-Hobson (H. W. Lee), British patent specification no. 224,425.

that a very small aberration patch for points off the axis resulted. This type of lens has been developed by Dr Ross in the United States of America and by H. W. Lee, in another direction, for the photography of stars for measuring their positions. In a lens made for the Cape Observatory of 35 inches focal length and including an angle of 40°, the mounting is interesting because it provides for free circulation of air so as to reduce the effects of differences of temperature on the system. The requirements of such lenses are that the star-images should be perfect circles, that is to say that the images of all points in the field must be quite free from coma and

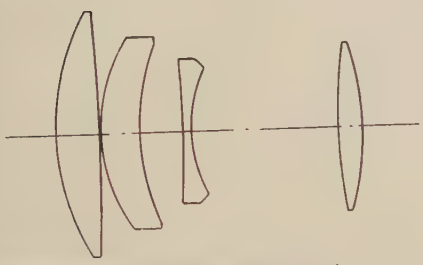

Figure 25. Ernemann, British patent specification no. 237,212.

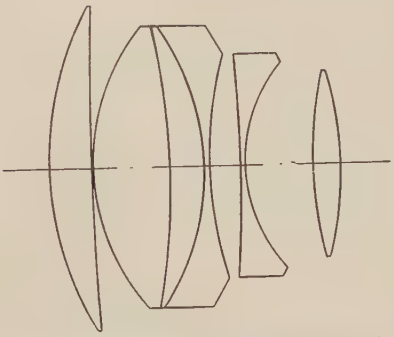

Figure 26. Ernemann, British patent specification no. 237,519.

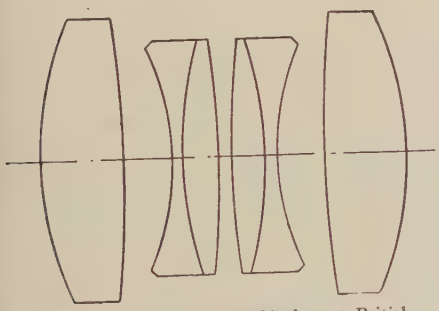

Figure 27. Meyer (Rudolph) plasmat, British patent specification no. 401,630.

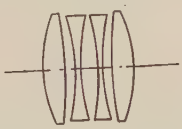

Figure 28. Taylor-Hobson (A. Warmisham) aviar, British patent specification, no. 113,590.

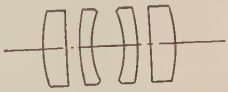

Figure 29. Busch omnar (K. Martin), British patent specification no. 19,504/01.

astigmatism, for the position of a star-image can be accurately measured only if the image is circular.

The quadruplet can be put into another form by making all the separate components simple meniscus elements. This was done in 1900 by H. Meyer[16] and in 1901 by K. Martin (of Emil Busch)[17] with an aperture *f*/6·8, figure 29. Lenses of this general form have since been extensively made by other manufacturers. When modified, it is particularly adapted to provide wide-angle lenses limited to small apertures.

Rudolph (of Zeiss) employing thicker dispersive components, figure 30, was able while satisfying the Airy-Petzval condition, to use shallower curves, and thereby the aperture was increased to *f*/3·5. This was the planar[18] which comes into class (*c*). In 1920 H. W. Lee[19] increased the aperture to *f*/2, figure 31. Recently

Zeiss[20] have increased the aperture to f 1·4, and Taylor, Taylor and Hobson[21] (H. W. Lee) to $f/1{\cdot}5$, while more recent constructions of Taylor, Taylor and Hobson, shown now for the first time, are due respectively to A. Warmisham, figure 32 (aperture $f/1{\cdot}3$)[22] and H. W. Lee[23], figure 33 (aperture f 1).

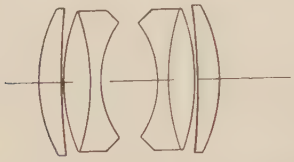

Figure 30. Zeiss (Rudolph) planar, British patent specification no. 27,635/96.

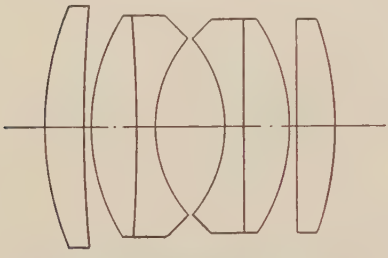

Figure 31. Taylor-Hobson (H. W. Lee), British patent specification no. 157,040.

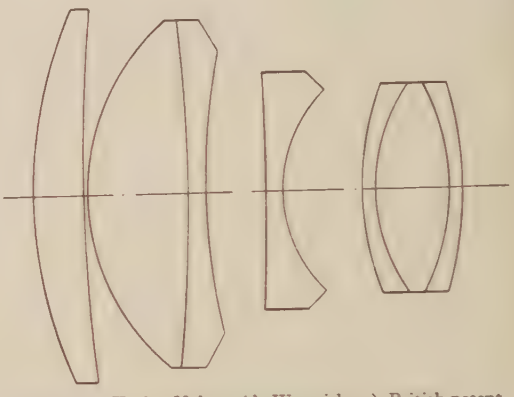

Figure 32. Taylor-Hobson (A. Warmisham), British patent specification no. 408,787.

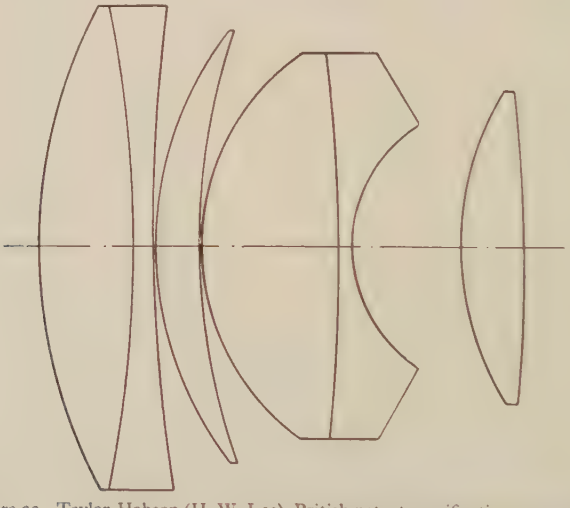

Figure 33. Taylor-Hobson (H. W. Lee), British patent specification no. 419,552.

§ 9. LENS OF VARIABLE FOCUS

Another problem arising from the demands of the cinema is the provision of a lens of continuously variable focal length. The cinematographer likes to vary the scale of his picture. This can be done discontinuously by applying to the camera a turret of lenses of different focal lengths, or continuously by placing the camera on

wheels and moving it about. But the advent of the sound film has rendered movement of the camera during action objectionable. The best solution of the problem is the provision of lenses of continuously variable focal length. In addition to others, references to which are lacking, Warmisham[24] has designed the lens illustrated in figure 34. The difficulties of design are both optical and mechanical. The optical system comprises three relatively movable parts of which the outside two, *A* and *B*, are dispersive and compound, and the inside part *C* is a large-aperture photographic lens. The lens system is drawn in continuous lines to indicate the position corresponding to its long focal length, and the members *A* and *B* are drawn also in dotted lines to show the positions which give the short focal length. When the lens is giving a short focal length there is a large angular field to be corrected, while in the long-focus position the aperture will be small unless the diameters of the lenses are made large, and such diameters would be enormous for the short-focus wide-angle position. Some compromise of aperture with long focus is therefore unavoidable. Mr Warmisham's lens has an aperture of *f*/3·5 at a focal length of 40 mm. and *f*/8 at a focal length of 120 mm.; a 3:1 ratio of scale is thus possible.

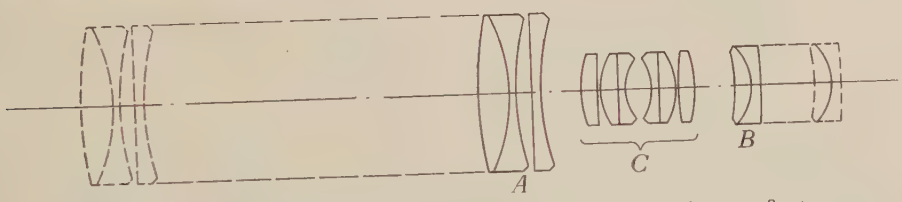

Figure 34. Taylor-Hobson (A. Warmisham) varo, British patent specification no. 398,307.

The mechanical difficulties are concerned with the cutting of precision cams to control the movements of the several components of the lens so as to maintain both the correction of aberrations and the focus on the film, as the focal length changes, and also to alter the iris diaphragm so that the *f* values remain correct.

§ 10. THE TELEPHOTO LENS

The telephotographic lens consists of a collective lens with a dispersive lens at such a distance behind it that the nodal planes are thrown right in front of the system, and the space between the lens and the focal plane is much reduced. Hence while the focal length may be large the camera is compact. The principle was first applied to telescopes in 1834 by Barlow and to photography in 1891, almost simultaneously in England (by Dallmeyer), France and Germany. In distinction from the normal type of lens of the time, with its field concave to the lens, the telephoto field was at first convex, its Airy-Petzval sum being over-corrected owing to the great separation between collective and dispersive components. The performance of these lenses was consequently poor. It was not until 1914 that the first anastigmat telephoto lens, figure 35 (aperture *f*/6), was made by Taylor, Taylor and Hobson under the British patent of L. B. Booth[25] and lenses of this construction were largely used in the War by the Royal Air Force.

Lee and Booth improved this lens by reducing the number of air-glass surfaces and increasing the aperture to f 4·5, the later Lee[26], by separating the collective component into two, figure 36, increased the aperture to f 3·3; and by separating the rear elements he corrected the distortion, a result which has not been achieved in any other telephoto lens. Figure 37 shows the Zeiss telephoto tessar lens[27], and figure 38 shows the Ross (Hasselkus and Richmond) telephoto lens[28].

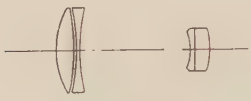

Figure 35. Taylor-Hobson (L. B. Booth) telephoto, British patent specification no. 3096/14.

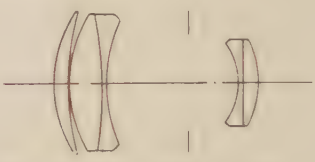

Figure 36. Taylor-Hobson (H. W. Lee), British patent specification no. 222,709.

Figure 37. Zeiss tele-tessar, British patent specification no. 179,529.

Figure 38. Ross (Hasselkus and Richmond) teleros, British patent specification no. 188,621.

§ 11. INVERTED TELEPHOTO LENS

By inverting the telephoto lens construction we get a system in which the nodal plane lies between the lens and the focal plane, i.e. the back clearance is greater than the focal length. This is sometimes an advantage when lenses of very short

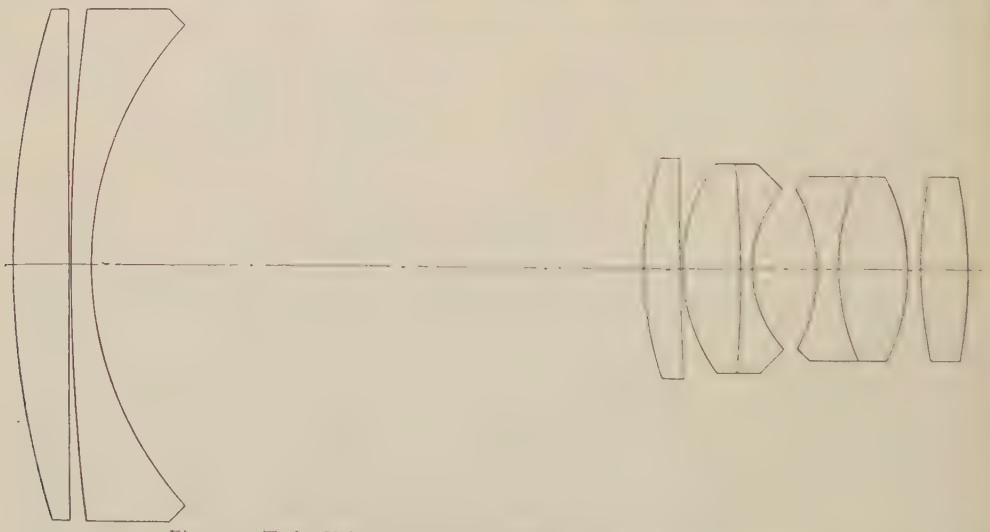

Figure 39. Taylor-Hobson (H. W. Lee), British patent specification no. 355,452.

focal length are needed; it is a necessity when space has to be provided behind such a lens, for example for the prisms used in some systems of cinematography in colour. This calls for a lens having not only abnormal back focus but also large

aperture and considerable field covered at the usual high standard demanded by cinematography. Various forms of inverted telephoto lens have been devised for both projection and photography: for projection by N. Bowen (translux)[29], and W. B. Rayton (of Bausch and Lomb)[30], the aperture being $f/2{\cdot}8$; and for photography, by H. W. Lee (Taylor, Taylor and Hobson)[31], in a lens having an aperture

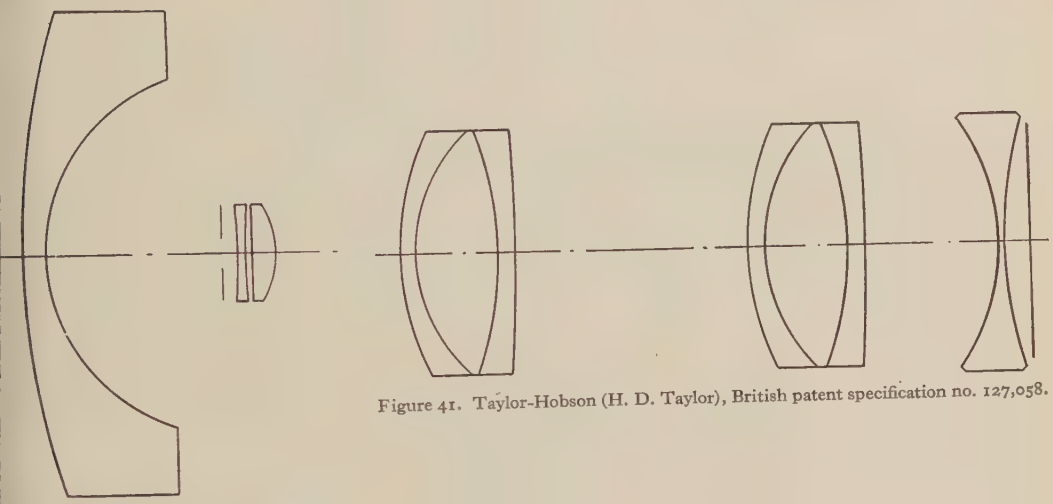

Figure 41. Taylor-Hobson (H. D. Taylor), British patent specification no. 127,058.

re 40. R. and J. Beck (R. Hill), British patent specification no. 225,398.

up to $f/2$, figure 39. The inverted telephoto type of lens has also been adopted by R. Hill and made by Beck[32], figure 40, in a lens for photographing the whole sky for meteorological purposes. The field is 180°, covered of course at an extremely small aperture.

§ 12. THE NEGATIVE FIELD-CORRECTOR

In 1866 Prof. C. Piazzi Smyth, the astronomer, suggested placing a dispersive (i.e. negative) lens *close to the focal plane* to correct the curvature of field of the Petzval portrait lens with which he was taking astronomical photographs. In this position the negative lens exerts its full corrective power on the Airy-Petzval sum while it has practically no effect on the focal length or on spherical aberration. So impressed was Piazzi Smyth with the possibility that he constructed a miniature camera, taking pictures 1 in. square, to photograph hieroglyphics inside the Egyptian tombs. This was the first high-speed miniature camera ever made, and was thus some sixty years before its time and suffered the usual fate of being too far ahead of the age. Piazzi Smyth's idea of field-correction was revived by Dennis Taylor in an $f/2$ lens[33], figure 41, made by T. Cooke and Sons and used at Mount Wilson Observatory for stellar photography. The Piazzi Smyth corrector is also now being applied by Dr Ross to the great new astronomical reflecting telescopes to adapt them for photography over a wider field than is otherwise attainable.

§ 13. FUTURE DEVELOPMENTS

This story has now reached the stage when to pursue it entails vision of the future.

No lens is perfect. When we say that aberrations are corrected we mean not that they are reduced to zero but that they are confined within some postulated circle of confusion, and that itself is imperfectly defined.

It seems unlikely that great advance on the present position can be made by adding further complexity to lenses of the types we have described as having become traditional. It may be that another genius (and we may hope again an English genius) may see a new and simplified solution of a problem which again has been pursued near to the limits set by complexity.

It may be that a solution will be discovered in the use of surfaces other than spherical, but that would not become practicable generally until we discovered means of producing and testing them during production and correlating the two surfaces of each element and the various elements with the requisite accuracy.

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(2) British patent specification no. 5194 1888.
(3) British patent specification no. 56,109/1890.
(4) British patent specification no. 19,509/1894.
(5) British patent specification no. 23,378/1892.
(6) British patent specification no. 16,640/1895.
(7) British patent specification no. 29,636/14.
(8) British patent specification no. 165,657.
(9) British patent specification no. 295,519.
(10) British patent specification no. 13,904 97.
(11) British patent specification no. 9528/1895.
(12) British patent specification no. 376,044.
(13) British patent specification no. 382,246.
(14) British patent specification nos. 350,323 and 383,591.
(15) British patent specification nos. 113,590 and 312,536.
(16) British patent specification no. 20,349/00.
(17) British patent specification no. 19,504/01.
(18) British patent specification no. 27,635/1896.
(19) British patent specification no. 157,040.
(20) British patent specification no. 297,823.
(21) British patent specification no. 397,281.
(22) British patent specification no. 408,787.
(23) British patent specification no. 419,552.
(24) British patent specification no. 398,307.
(25) British patent specification nos. 3096/14 and 139,719.
(26) British patent specification no. 222,709.
(27) British patent specification no. 179,529.
(28) British patent specification no. 188,621.
(29) British patent specification no. 348,123.
(30) U.S. patent specification no. 1,934,561.
(31) British patent specification no. 355,452.
(32) British patent specification no. 225,398.
(33) British patent specification no. 127,058.

DEMONSTRATION

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Apparatus for Measuring the Viscosity of Liquids at High Pressures. *Demonstration given on December* 7, 1934 *by* C. C. Mason, O.B.E., M.A., F.Inst.P., *by the courtesy of the* Burmah Oil Company, Ltd.

The formula used in calculating the viscosity from the velocity of the sinker is that due to Lawaczeck. It contains terms showing that the velocity is proportional to the cube of the clearance between sinker and tube, and directly proportional to the difference in density between sinker and liquid. It is thus possible with several sinkers to cover a large range of viscosities. Four are provided having radial clearances of 0·6, 0·8, 1·0 and 1·25 mm. The sinkers are of brass and are hollow, but are made to receive a maximum of four tungsten weights. It is therefore possible to change the effective density, with the result that with the four sinkers viscosities between 10 and 500 centipoises can be determined.

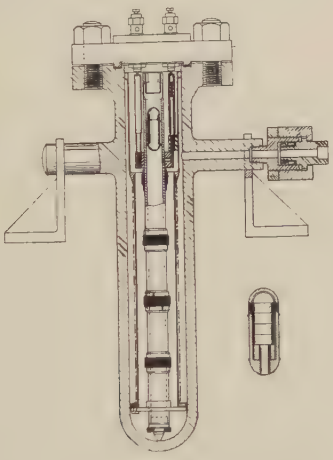

Figure 1. Sectional view of the apparatus.

The inner brass tube is surrounded by another tube inside the steel tube. This intermediate tube carries a resistance mat, and is designed to encourage convectional circulation when current passes through the mat. Connexions to this and to the coils are brought in through the cover by means of an arrangement similar to a sparking plug. A vapour-pressure thermometer shows the temperature and, being provided with an adjustable contact, permits control of the temperature through the medium of a relay.

In the demonstration the image of the galvanometer string was projected on to a screen, and when the instrument was inverted the four deflections were observed as the sinker passed through the four coils.

The instrument is primarily for the purpose of determining the pressure coefficient of viscosity of liquids, and particularly of the mud mixtures used in the boring of oil wells. Heating-arrangements are included in the design in order that temperature effects also may be investigated.

The fundamental principle is not new and consists in measuring the velocity of fall of a cylindrical sinker with spherical ends, under gravity, in a tube. This inner tube is of brass and is quite incapable of supporting the pressure of 4000 lb./in.^{2} which will be used. It is therefore enclosed in an outer steel tube. This is filled

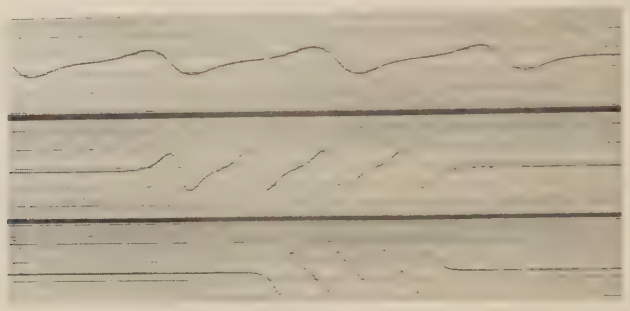

Figure 2. Typical records (reduced to half size).

with oil and has a connexion to a pressure pump, and the pressures are communicated to the contents of the inner tube through a rubber diaphragm at one end. The outer tube has trunnions so that it can be inverted for the fall of the sinker. The movements of the sinker cannot be followed visually, and this difficulty is surmounted by the method that is used to measure the velocity of a projectile from a gun, although in the present case the velocities and dimensions are small. A small piece of cobalt magnet is inserted in the sinker, and on the outside of the tube are four coils equally spaced 7·5 cm. apart. These are connected in a series-parallel arrangement to a small permanent-magnet string galvanometer, and as the sinker passes through each coil the galvanometer string is deflected. The deflections are recorded photographically by means of a falling-plate camera, time lines being put on the record by momentarily interrupting the light through the galvanometer every tenth of a second with spokes on the rotor of a small synchronous motor driven from a.-c. mains.

REVIEWS OF BOOKS

Introduction to Atomic Spectra, by H. E. WHITE, Ph.D. Pp. xii+457. (New York and London: McGraw-Hill Publishing Co., Ltd.) 30*s*. net.

Practically every account of atomic spectra which has appeared in the last ten or twelve years is either too brief or too highly mathematical and theoretical for those about to take up the subject for special study. Dr White, a member of the team of very distinguished spectroscopists in the University of California at Berkeley, therefore set out to produce for such students an account to which neither of these objections could apply, and he has succeeded most admirably. This excellent book is highly recommended both to beginners and also to those who are already familiar with parts of the subject; and it is the only book of which the reviewer is able to say this so unreservedly and so cordially.

Each section of the subject is opened as nearly as possible at the very beginning, logically developed, and unsparingly illustrated with excellent diagrams and spectrograms. One of the most satisfying features of the work is that the spectra themselves are never lost sight of for longer than is necessary. Short tables of selected observational data are given in the text wherever examples are required for further clarity of the discussion. Any attempt to include exhaustive numerical data, even for one atom or one group of atoms, would obviously be out of place in this new volume of the *International Series*, which already includes Bacher and Goudsmit's recent book of data on *Atomic Energy States*. These two volumes might well be regarded as two parts of a single treatise, almost indispensable to the present-day spectroscopist.

In the well-founded belief that the student can best understand the newer quantum mechanics through a thorough acquaintance with the spectra themselves and the Bohr-Sommerfeld orbits and the vector model, Dr White devotes the opening chapter to the early empirical analysis of line spectra, then develops the older and newer quantum theories of atoms having one valency electron (chapters II–X), and afterwards deals with the more complex spectra of atoms having two or more valency electrons (chapters XI–XV). In the later chapters (XVI–XXI) accounts are given of X-ray spectra, iso-electronic emitters and their spectra, hyperfine structure, perturbations, the Stark effect, and the breadths of lines. The book is well indexed.

The printing too is excellent; in only one respect, so far as the reviewer has yet noticed, could a slightly better setting be suggested: an exponent might be printed after, rather than directly above a subscript; e.g., "$n_2{}^2$" and "$Z_0{}^2$" rather than "n_2^2" and "Z_0^2". Perhaps two other matters in which some readers may not quite agree with the author might be mentioned. First, such an expression as "11 wave numbers" (p. 36) is not a good alternative to "11 wave-number units" or "11 $cm.^{-1}$"—in the analogous case nobody would say "11 wave-lengths" instead of "11 A.U.". Secondly, as to the discovery and naming of the *fundamental series* (pp. 6 and 9) the late Prof. Hicks pointed out in his *Treatise*, and several times in conversation, that *fundamental* (which he first used in the sense *hydrogen-like* or *Balmer-like*) is just a name for which there is neither more nor less to be said than for the other names *principal*, *sharp* and *diffuse*; to call them *Bergmann series* seemed to do scant justice to Saunders's earlier recognition of the Cs doublets or to Runge's and Ritz's discoveries of the connection with the D term. Two or three minor slips also might be mentioned. The last line of p. 25 should read "2 for ionized helium". Of the three sections of Rowland's map mentioned on p. 2, only two appear in figure 1.2; the section including the sodium D lines is omitted; and the section which purports to show the *E* lines (of iron and calcium) is cut off just too short to include these, but has as its most prominent feature the *b* triplet of magnesium, which, moreover, is incorrectly lettered as *E* in figure

1.1; again "*H* lines" in the top line of p. 3 should be "*H* and *K* lines". A second edition will, no doubt, afford Dr White an early opportunity of setting these matters right, for his book will surely be a standard work for many years to come. W. J.

The Structure of Spectral Terms, by W. M. Hicks, Sc.D., F.R.S. Pp. xi+209. (London: Methuen and Co., Ltd.) 10*s.* 6*d.* net.

The late Prof. Hicks's studies in spectroscopy were directed to the discovery of numerical relations between the wave-numbers of atomic spectrum lines and terms with little or no reference to matters concerning current theory of atomic structure. These studies extended over the last twenty-five or more years of his long and active life. When, in the early summer of last year, he was seized with illness which proved fatal (he died on August 17, within five weeks of his 84th birthday), the proof sheets of this his last work had only just been received and the proof-reading had hardly begun. In this formidable task he was to be assisted by Mr J. R. Clarke, one of his old students and now Lecturer in Physics at the University of Sheffield, from which Dr Hicks retired in 1917. Prof. S. R. Milner therefore joined Mr Clarke in the remaining stages of the work.

In this book Dr Hicks has considerably extended the results set out in his earlier and larger *Treatise on the Analysis of Spectra*, which appeared about the same time as Prof. Fowler's *Report on Series in Line Spectra* and Paschen and Götze's *Seriengesetze der Linienspektren* in 1922 and is now out of print. The opening chapter deals with the representation of line series by formulae, and includes, as a very useful and instructive example, the evaluation of the four constants of the more general of Dr Hicks's two modifications of the Rydberg formula; these two formulae, it may be noted, are still widely regarded as the most useful and accurate of the many which have been proposed for this purpose. In the following chapters a large amount of new observational evidence is presented concerning special features of Dr Hicks's empirical analyses such as satelloids, high-order emission lines, on relations between multiple terms, collaterals, linkages, and summation lines. In the ninth and last chapter atomic structure is discussed in relation to the results of the foregoing analyses. As is to be expected from the very nature of the work and the large amount of numerical material handled, the book is not an easy one to read. It is excellently printed and, in conjunction with his former *Treatise*, forms a fitting record of Dr Hicks's long, painstaking and enthusiastic research in this branch of spectroscopy.

W. J.

Resonance Radiation and Excited Atoms, by A. C. G. Mitchell and M. W. Zemansky. Pp. viii+338. (Cambridge University Press, The Cambridge Series of Physical Chemistry.) 18*s.* net.

This book, by two workers in the field, fills an obvious gap in the literature of experimental optics. It begins with an introductory chapter on line spectra and the elementary processes involved in resonance radiation, followed by a very useful account of typical light-sources appropriate to their experimental investigation. The second chapter deals with stepwise radiation and with physical and chemical effects of collisions with excited atoms. In chapter III absorption lines are discussed in detail, and an account is given of the measurement of the durations of excited states. Chapter IV, on "Collision processes involving excited atoms", deals rather fully with the broadening of absorption lines and with quenching. The final chapter, on the polarization of resonance radiation, gives a comprehensive account of the effects of magnetic fields, and a brief account of those of electric fields, on the radiation.

The book will be an indispensable work of reference to all who are seriously interested in the subject, and the bibliographies are remarkably up to date. The theory is in places a little too severely compressed, and the theoretical sections are rather dispersed among

the experimental descriptions, so that the book will make difficult reading for the unaided beginner, but taken as a whole it is one upon which the authors are to be warmly congratulated and thanked.

H. R. R.

The Diffraction of Light, X-rays and Material Particles, by C. F. Meyer. Pp. 473. (University of Chicago Press.) 22*s.* 6*d.*

This is a book of a rather unusual type; it consists of a detailed exposition of the phenomena of diffraction treated with as little mathematical apparatus as possible. It may be said at once that it is extremely well done; the explanations are clear, the style easy and sympathetic. In addition, the author has given historical information which is much fuller than that usually given in text-books and which adds considerably to the interest. He deals fully with a number of points usually omitted, such as the apparent source of light diffracted from an edge, and his treatment of, for example, the distinction between the Fresnel and Fraunhofer classes of effects, and of Babinet's principle, is unusually thorough and careful. The methods of mounting the plane and concave gratings and the errors of gratings are dealt with at considerable length.

It is probable that an English student who is advanced enough to want such a detailed account of one aspect only of wave theory would be able to grasp a more mathematical treatment and would save time by doing so. On the other hand, many capable students find difficulty in grasping the rather difficult physical principles underlying the mathematics, and for these the book will be very valuable. In addition it should be said that many of the more mathematical questions are dealt with in appendices.

The second part of the book, dealing with X-rays and de Broglie waves, is considerably more detailed, at least on the experimental side, than would be required by most honours students. As the preface explains, it is intended largely for workers in other sciences whose field requires knowledge of these matters, and to this purpose it is well suited. In addition to describing the main experiments on electron-diffraction, the author gives a clear account of the very interesting work of Stern and others on the diffraction of atoms and molecules.

G. P. T.

Newton and the Origin of Colours, by Michael Roberts and E. R. Thomas. Pp. viii + 133. (London: G. Bell and Sons.) 3*s.* 6*d.* net.

It is a pleasure to be able to give an unqualified recommendation to this well-written little book. It makes no pretence of giving an exhaustive account of Newton and his work on colour, but aims rather at a brief sketch of some of the formative influences surrounding his early life, and of the simpler methods of his optical researches. We are given some glimpses of his contemporaries and their comments on his work; and the whole account is used to illustrate the various principles of scientific method and their evolution.

It can be heartily commended as a corrective to any over-dose of technical study, and the present reviewer intends to bring it to the notice of his own students. It is just long enough and sufficiently detailed to create interest, and not so omniscient as to crush discussion. (How often authors fail to hold such a balance!) There are one or two technical queries, as for example "he added to the water *a little* sugar of lead to raise its mean refractive index sufficiently to make it equal to that of glass" (the italics are the present writer's), and the possible misinterpretation of the term "spherical aberration" on p. 38. If indeed it is the case that the aberration now known as "distortion" was originally termed "spherical aberration", some reference in support of this would be of interest. It would be idle, however, to suggest that such insignificant defects as these detract in any way from the success of the book.

If there is any critical feeling left after its perusal, it may be that this "closer" view of Newton's work hardly gives a sense of the real magnitude of his achievements. In a book

bearing the above title, some fuller mention might well have been made of his work on colour-mixture, and of the remarkable colour diagram which has formed the foundation of modern methods of colour measurement, and played no small part in the development of the most fruitful theory of colour-vision.

It is doubtful too whether his brilliant achievement in grinding a relatively large-aperture paraboloid has ever received the praise it merits. The figure must indeed have been excellent to allow of the results actually obtained in his reflecting telescope, and little seems to be known of his methods of working mirrors.

However, where so much of interest has been collected in so small a compass, it would be ungenerous to ask for the full discussion of the work of this remarkable man, many of whose sayings bear a freshness and relevance to problems of our own day which is nothing short of amazing. L. C. M.

Luminescence des Corps Solides, by MAURICE CURIE. Pp. 146. (Recueil des Conférences-Rapports de Documentation sur la Physique, vol. XXIV.) (Paris: Les Presses Universitaires de France.) 50fr.

This recent addition to a deservedly famous series of monographs on various branches of modern physics deals with a vast and fascinating subject to the development of which both physicists and chemists have contributed papers almost innumerable. Comprehensive accounts of it, with extensive bibliographies, have appeared from time to time, e.g. in Kayser's *Handbuch der Spektroscopie*, volume **4** (1908), the National Research Council's Bulletin *Luminescence* (1923), Pringsheim's *Fluorescenz und Phosphorescenz* (1928) and Lenard, Schmidt and Tomaschek's volumes **1** and **2** of the Wien-Harms *Handbuch der Experimentalphysik* (1928). The last-named contains a particularly complete account of the extensive and important work of Lenard and his school. The present report by a notable contributor to knowledge of these phenomena will, without doubt, be very welcome to those who require a concise account of the present state of affairs. It is confined, it is true, to one branch of the subject, namely the luminescence of inorganic solid solutions. These consist, in general, of a crystalline substance, the *diluent*, of low electrical conductivity (such as the sulphides of Zn, Ca, Sr, Ba), containing, as an impurity, a certain, often very small, proportion of the *centre*, i.e. a metal of relatively high atomic number (such as Bi, Cu, Mn, Ni, Pb). Besides this class, of which CaS(Bi) is an example, we also have sulphide mixtures such as ZnS.CdS(Cu), oxides such as CaO(Sm), halides such as KCl(TlCl) and many other compounds. Fluorescence and phosphorescence excited by visible or ultra-violet radiation have been investigated far more extensively than those excited by cathode rays, X-rays, α, β and γ rays, and other means. Accordingly photoluminescence (chapter 1) occupies about two-thirds of the book, and is followed by much shorter accounts of cathodic luminescence (chapter 2), radioluminescence and radio-photoluminescence (chapter 3), triboluminescence and scintillations (chapter 4) and luminescence of solids in flames (chapter 5). A further volume is promised which will treat of the luminescence of gases and vapours, organic substances, and certain inorganic crystalline substances which, unlike those dealt with in the present volume, are in a state of purity. W. J.

Electrons (+ and −), Protons, Photons, Neutrons, and Cosmic Rays, by R. A. MILLIKAN. Pp. x+492. (London: Cambridge University Press.) 15*s*. net.

Most undergraduate students of physical science have diligently thumbed Prof. Millikan's admirable survey entitled *The Electron*. This volume appeared in 1917, and in revised form in 1924. The present work may be regarded as a third edition of *The Electron*, and, without departing from the historical mode of presentation which gave unity to the older volume the author has been able to make his present volume a thoroughly up-to-date survey of the subject by adding six chapters which deal respectively with waves and

particles, the discovery of the cosmic rays, the spinning electron, the positron, the neutron and transmutations of the elements, and the nature of the cosmic rays. The new volume, which gives a view of the position of a most rapidly changing science as it appears at the end of 1934, will be as valuable to the new generation of students as its predecessors were to an older generation.

The name of the author attests sufficiently the manner of presentation.

Actualités Scientifiques et Industrielles. (Hermann and Co., 6 Rue de la Sorbonne, 6, Paris.)

Under the above general heading we have received the monographs listed below. Each is written by an authority on his subject and the treatment is, in general, concise and clear.

115. H. Mineur. *Histoire de l'Astronomie Stellaire.* 15 fr.
116. H. Mineur. *Éléments de Statistique Mathématique.* 12 fr.
141. H. Mineur. *Photographie Stellaire.* 18 fr.
147. Pierre Humbert. *Le Calcul Symbolique.* 10 fr.
159. L. Brillouin. *Les Champs "Self-Consistents" de Hartree et de Fock.* 10 fr.
160. L. Brillouin. *L'Atome de Thomas-Fermi.* 12 fr.
162. P. Swings. *Travaux récents sur les molécules dans le Soleil, les Planètes et les Étoiles.* 14 fr.
177. J. Genard. *Fluorescence des Vapeurs dans le Champ Magnétique.* 12 fr.
181. Louis de Broglie. *Une Nouvelle Conception de la Lumière.* 12 fr.
182. Irène Curie et F. Joliot. *L'Électron Positif.* 10 fr.
185. M. Haïssinsky. *Les Radiocolloïdes.* 9 fr.

Chemical Kinetics and Chain Reactions, by N. Semenoff. (International Series of Monographs on Physics, edited by R. H. Fowler and P. Kapitza.) Pp. xii + 480. (Oxford: The Clarendon Press, Mr Humphrey Milford.) 1935. 35*s.* net.

The foundations of chemical kinetics, or the theory of the velocities of chemical changes, were laid by the researches of Harcourt and Esson about 1850–66, but the subject was first systematically formulated by van't Hoff in his *Études de Dynamique Chimique* in 1884, who obtained equations for uni-, bi- and multi-molecular changes and gave a simple kinetic interpretation to them. The effect of temperature was expressed in the form $k = Be^{E/RT}$, where k is the velocity constant, B and E are constants, R is the gas constant and T the absolute temperature. Arrhenius in 1889 showed that E may be interpreted as an energy of activation, such that only molecules with an energy exceeding E are capable of undergoing change. Succeeding investigation has, until recently, been mainly concerned with the application and elaboration of these fundamental laws.

As more and more systems were investigated, it became clear that the number of reactions which proceed normally is surprisingly small, and this number is constantly decreasing so that, whereas bimolecular reactions were formerly regarded as the predominant type, a recent monograph on the subject could record only two unequivocal cases of bimolecular reactions.

The idea of a reaction chain appeared about 1913. In one formulation it assumes that the chemical energy set free in a single molecular process ('elementary act') is not directly transformed into heat, but may be consumed at least partly in the formation of intermediate products with high energies which, by interaction with the original substance, are constantly renewed at the expense of the released energy. A simple case of such a chain reaction is afforded by the photochemical union of hydrogen and chlorine. The absorption of one quantum by a chlorine molecule produces, according to Einstein's law, an elemen-

tary act leading to the formation of two atoms of chlorine. Each chlorine atom then takes part in a cycle of changes represented by the equations

$$1. \quad Cl_2 + h\nu = Cl + Cl;$$

$$2. \quad Cl + H_2 = HCl + H;$$

$$3. \quad H + Cl_2 = HCl + Cl;$$

and the chain of reaction thus proceeds until it is terminated by collision of a chlorine or hydrogen atom with an oxygen molecule, for example, or with the wall of the vessel.

The theoretical and experimental investigation of chain reactions has been the object of intensive study in recent years, and more than half the material in the book has been gathered in the last four years, a substantial part of it being done in the author's laboratory in Leningrad. The first part of the book deals with the general principles of the chain theory, together with the straightforward mathematics involved. The other three parts contain a detailed and critical analysis of the experimental data for nearly fifty reactions on the basis of the theory, and finally a summary of the main conclusions reached.

Such a survey by a leading authority is of very considerable value, particularly as the subject is one on which much work in various fields is now in progress. It is obviously impossible to specify the various reactions considered, but it may be mentioned that they include the classical hydrogen-chlorine reaction, the glow of phosphorus and the oxidation of hydrogen, carbon monoxide and hydrocarbons—all reactions which have been studied over a long period of years and still present obscure features. Prof. Semenoff's work is one which brings together in a very critical and instructive way a large mass of scattered information, and its appearance is an event which will be welcomed both by the specialists in this field and by the larger body of scientists who are desirous of finding out what progress has been made in recent years in the study of these very fundamental problems.

J. R. P.

Some Problems of Modern Meteorology. Pp. v + 170. (London: Royal Meteorological Society, 49 Cromwell Road, S.W. 7.) 3*s*. 6*d*.

This book consists of sixteen articles by fourteen authors, on some of the main problems of meteorology. These articles are reprinted, with some additional notes, from the *Quarterly Journal of the Royal Meteorological Society*, where they originally appeared during the period July 1930 to October 1934, under the editorship of Prof. D. Brunt, who contributes an introduction to the present volume. The subjects discussed are the origin of cyclonic depressions, radiation and absorption in the atmosphere, energy-transformations in the atmosphere (Brunt), weather-forecasting, rainfall (Douglas), origin of anticyclones, post-glacial climates and the forests of Europe (Brooks), the atmospheric circulation (Barlow), thunderstorms (Watson Watt), atmospheric turbulence (Davies and Sutton), seasonal forecasting (Normand), antarctic meteorology (Kidson), terrestrial magnetic variations (Goldie), meteorological acoustics (Tucker), condensation in the atmosphere (Bennett), and atmospheric ozone (Dobson and Meetham). The articles summarize the present position of these problems, and give numerous recent references to work upon them.

The collected re-issue of these articles should appeal not only to meteorologists, who should in general have read them in the *Quarterly Journal of the Royal Meteorological Society*, but also to a much wider circle of physicists who do not see that journal. The latter will, it is hoped, be impressed by the great body of meteorological knowledge which underlies these articles, and no less impressed and interested by the fundamental character of many of the chief unsolved problems of the subject.

The extremely moderate price of the book should be noted.

S. C.

Thermostats and Temperature-Regulating Instruments, by ROOSEVELT GRIFFITHS, M.Sc. (London: Chas. Griffin and Co., Ltd., 1934.) 10*s.* net.

It is perfectly true that an instrument is a means to an end, and that the end should not be lost sight of in contemplating the means. Nevertheless among the devotees of experimental science one may find here and there a few favoured souls who take an artist's delight in an instrument for its own sake, who realize fully that the first duty of the instrument is to do its job, but whose interest slackens a little when they are asked to transfer their attention from the instrument to the job which it is doing. Whatever may be the bent of the author of this book there is no doubt that he is a lover of instruments. His descriptions of the various thermostatic devices are full, lucid and written *con amore*.

He has covered a wide range, and has described thermostats based on the temperature expansion of solids, of liquids and of gases, on the boiling-points of liquids, and on change of resistance with temperature. He has provided chapters dealing with the bimetallic and contact types of regulator, and with potentiometric and induction regulators. The last chapter of the book deals with low-temperature control. The volume is well produced and illustrated, and is compact in size and reasonable in price. It should prove a useful addition to the shelves of the experimenter. A. F.

Principles of Mathematical Physics, by W. V. HOUSTON. Pp. xi+265. (London: McGraw-Hill Publishing Co., Ltd., 1934.) 21*s.* net.

This book is so condensed that it could be of little use except as a class-book where the lecturer proposes to cover practically the same course as that outlined in it. A feature is the large collection of problems, many of which we are more accustomed to seeing as theorems. Thus the student is given the problem of the brachistochrone as exercise 2 of chapter 5, and elsewhere is asked to find the field inside a spherical cavity and also inside long and short cylindrical cavities hollowed out in a block of magnetic material placed in a magnetic field. From the equation $E=mc^2$ he is asked to compute the mass of a moving electron, remembering that owing to the Lorentz transformation it becomes an ellipsoid of revolution. These examples suggest that the author is contemplating readers who will not be troubled by purely mathematical difficulties; yet apparently he envisages readers who need instruction in quite elementary differential equations, to which chapters 1 and 3 are devoted. Indeed, quite a considerable part of the book deals not with mathematical physics but with physical mathematics. In addition to the chapters just mentioned, there are others on the calculus of variations and on vector analysis, which really belong to the realm of mathematics. There is good reason for the inclusion of the one on variational methods, because there are few elementary treatments of this subject available. The chapter on vectors, again, is valuable for its last few sections, on the linear vector operator and on Gibbs's dyads; the relation to tensor calculus is shown, and use is made of these ideas elsewhere in the book, particularly in treating rigid dynamics by means of Euler's angles.

The part of the book devoted to true mathematical physics restricts itself to non-quantum physics; it is none the worse for this, since the main mathematical points which the student will need later in quantum theory have been rather ingeniously introduced in the treatment of the classical theory. The subjects dealt with are mechanics up to the Hamiltonian equations (but not elasticity or hydrodynamics), the first two laws of thermodynamics, statistical mechanics (14 valuable pages), electricity, and the restricted theory of relativity. A particularly good chapter is that on the theory of vibrating systems in general, where a digression is made to discuss the expansion of functions in series of orthogonal functions. On the other hand, it is a pity to see the author apologizing to the student for dealing with the mechanics of rigid bodies, and admitting that they do not

exist in nature. Actually even a liquid is a rigid body, as far as the equations of mechanics are concerned, if its volume and shape are not changing.

The book is well printed and singularly free from misprints, except on p. 166 where the last few lines have no connection with the matter immediately preceding or following them.

J. H. A.

Relativity Physics, by W. H. McCrea, M.A., B.Sc., Ph.D., F.R.S.E. Pp. vii + 87. (London: Methuen and Co., Ltd., 1935.) 2*s.* 6*d.* net.

This short monograph gives an admirable account of those results of the special theory of relativity which find most frequent application in physics. There is no other book, as far as the knowledge of the reviewer goes, which contains in such an accessible and concise form the wealth of information which is provided here by Dr McCrea. After a brief account of the origin of the Lorentz transformation the author applies the special theory of relativity to numerous problems of kinematics, mechanics, optics, electromagnetic theory, atomic physics, thermodynamics, statistical mechanics and hydrodynamics. This is an amazing array of topics and every student of the theory of relativity will be glad of such a concise and simple summary of the principal results which have been obtained in these widely different fields by relativistic methods.

The only notable omission is the lack of any reference to the use which was made by L. H. Thomas of the Lorentz transformation in calculating the precession of a spinning electron moving through an electric field. This investigation has a considerable historic interest both in relation to the quantum theory of the anomalous Zeeman factor and in relation to relativistic rigid dynamics.

The mention of rigid dynamics suggests another small criticism which can be urged against this monograph. It deals exclusively with the successes of relativistic theory and makes no reference to its failures. Thus it does not refer to the many unsuccessful attempts to construct a relativistic dynamics of rigid or quasi-rigid bodies, and it does not refer to the, as yet, unresolved problem of the relativistic dynamics of a system of particles. The only reference to this topic is on p. 79, lines 4 and 5, where it is asserted that Hamiltonian equations of motion hold good in relativistic mechanics. There is a reference to the equations deduced on p. 28. However, these equations refer to a single particle only and all attempts to construct a Hamiltonian function for a system of several particles have so far met with complete failure. The difficulty is probably due to the inapplicability of the special theory of relativity to any systems except isolated particles. Thus Eddington has recently asserted the need for reintroducing the concept of absolute simultaneity when discussing the properties of a complex system.

However, these detailed criticisms are entirely of a minor character and do not detract in any way from the great value of this little book as a most valuable summary of standard results.

G. T.

Solid Geometry, by L. Lines. Pp. xx + 292. (London: Macmillan and Co., 1935.) 6*s.*

The disadvantage in allowing one who is not a practising teacher of mathematics to review this book is that the reviewer is not sure where to apportion his praise. The book is intended primarily for the use of pupils preparing for one of the Higher School Certificate examinations, and thus gives a course in solid geometry which would frequently be taken by those not destined to become mathematical specialists. From this point of view, the advance on the methods of twenty years ago is enormous and somebody should be highly congratulated. If Mr Lines is leading the way, let him accept the felicitations; if he merely follows others, then we must regret that the pioneers have not been more widely acclaimed.

The solid geometry dealt with is the Euclidean geometry of the point, line and plane,

extended so as to make use, where advisable, of algebraic and trigonometric methods. It is not 'experimental' geometry, and on the other hand it does not overlook the value of suitably drawn diagrams. The striking differences from the older books lie in the subject matter, and the use made of modern ideas in notation. To take the latter first, we can illustrate it with part of the rider "If three planes intersect, two by two, show that their lines of intersection are either concurrent or parallel".

Let the three planes be α, β, γ. The straight lines $\gamma\alpha$ and $\alpha\beta$ lie in the same plane α; $\therefore$ they either intersect or are parallel.

If they intersect, their common point lies on all three planes; i.e. it is $\alpha\beta\gamma$;

$\therefore$ it lies on $\beta\gamma$

$\therefore$ $\beta\gamma$, $\gamma\alpha$, $\alpha\beta$ are concurrent."

The way the notation assists the argument is well brought out even to a young pupil.

As regards the subject matter, after the more usual geometry and mensuration we come to a detailed treatment of polyhedra, including the star polyhedra, and it is pointed out that Euler's theorem breaks down for certain of the latter. These chapters are followed by extremely good treatments of subjects suggested by physics—space lattices and their classification, and sphere-packs—and the book is brought to a close with a chapter on patterns and crystals. Perhaps the only thing to regret is the absence of some elementary introduction to geometry on the surface of a sphere.

A question arises whether the average young student will find the nomenclature too much strain on the memory. The first page of the excellent index includes *anorthic*, *bisphenoid*, *Bravais*, *clinographic*, *reguli*, *snub* (cube), *cuboctahedron*, *dyakis*, *stellated* (dodecahedron) and *enantiomorphous*, all of them words which would be new to most pupils.

J. H. A.

Cambridge Tracts in Mathematics and Mathematical Physics, No. 32. *Generalized Hypergeometric Series*, by W. N. Bailey. Pp. 108. (London: The Cambridge University Press.) 6*s*. 6*d*. net.

The latest of the *Cambridge Tracts in Mathematics and Mathematical Physics* is devoted to generalized hypergeometric series. This is a subject in which most of the developments of the last few years have been made by the author, Dr W. N. Bailey. He has skilfully arranged his material so as to display the variety in the methods which are available for obtaining the numerous formulae which have been discovered.

A hypergeometric series is a generalization of the binomial expansion. Binomial coefficients can be found in succession by multiplying by fractions, the numerators and denominators of the fractions being increased successively by unity. Multiply each term by two such fractions and the hypergeometric series is obtained. Multiply by three or more such fractions and the resulting expansion is a generalized hypergeometric series. It is well known that certain hypergeometric series are related to each other in simple ways. In some cases the series can be summed, just as a binomial expansion can be summed. The more general theory is concerned with the discovery of relations between generalized hypergeometric series and with their summation, which is usually in terms of gamma functions.

It has been found possible to classify the generalized series; the most interesting type is the "well-poised" series in which each of the fractions used for multiplication at any stage of the generation of the series has the same value for the sum of numerator and denominator. Bailey has actually found formulae relating to well-poised series of the ninth order, i.e. series in which there are no fewer than nine fractions to multiply by at each stage.

The subject has many points of contact with the theory of the functions used in mathematical physics and, although the more elaborate formulae in the tract have not yet

found any application, it may prove useful to physicists to have such formulae readily available. There is one application which has not yet been made explicitly, though the cell for it was announced in 1858 when Cayley published a short article in the *Philosophical Magazine* and enunciated a proposition which he had not been able to prove but which he said he had discovered in discussing certain relations in planetary theory. A proof of Cayley's theorem was published by Orr in 1899 and it is now known how the theorem fits into the theory of generalized hypergeometric series, but it is not known whether there is an important application in planetary theory. It is to be hoped that some expert in that subject will look into the question. F. J. W. W.

Numerical Studies in Differential Equations. Vol. 1, by H. Levy and E. A. Baggott. Pp. viii+238. (London: C. A. Watts and Co.) 12*s.* 6*d.*

All who were present at the fascinating lecture given by Prof. Levy to the London Mathematical Society on May 19, 1932, have been looking forward ever since to the appearance of his promised book on the numerical treatment of differential equations. The present instalment, volume **1**, tends rather to whet the appetite for what is to come than to slake the thirst. Here we have an expanded treatment of the purely graphical methods and of the usual numerical processes of the type devised by Runge. Picard's method for obtaining a series solution (not necessarily in integral powers of the independent variable) is also included, and is made to appear much more attractive than most writers have made it.

The familiar methods of integrating ordinary differential equations numerically practically restrict themselves to the case when the boundary conditions consist in the assignment of definite values to the dependent variable and all but the highest of its differential coefficients, at a point which may be taken as origin. This book does not shirk the more difficult problems which arise when boundary conditions are assigned at two or more points in the range of integration, and it is in this respect that it will be most valuable.

The treatment is very clear throughout. As befits the subject, processes and methods are frequently expounded not by giving general investigations but by applying them to specific numerical problems. In addition, an adequate selection of examples for practice is included.

The last chapter contains a variety of miscellaneous theorems which do not strictly belong to the subject of numerical treatment, though their applicability to that subject is illustrated—in striking fashion on occasion. Here we are reminded by meeting the characteristic values of a parameter, that the second volume is to deal systematically with partial differential equations. This will be a difficult task, but the manner in which volume **1** has been carried out suggests that the right authors have been found for the work.

J. H. A.

Mathematical Tables. Vol. 3.* (*Minimum Decompositions into Fifth Powers.*) By L. E. Dickson. (London: Office of the British Association, 1933.) 10*s.*

The theorem that any integer can be expressed as the sum of not more than four squares has long been known, but there is no corresponding theorem for powers higher than the square. In the case of the fifth powers, for example, it is evident that 31, being less than 2^5, cannot be decomposed into fewer than 31 such terms, whilst 223 (which is less than 3^5) requires 37, viz. $(6\times 2^5+31\times 1^5)$.

The present table shows the actual minimum decompositions of all numbers up to 150,000 and the minimum number of fifth powers to be added together to make any number up to 300,000. Thus the entry

87701	1 0 5 1 6 0 1

* In the review of volume 2 of this publication, *Proc. phys. Soc.* 45, 133 (1934), "volume 3" was printed in error for "volume 2."

means that $87701 = 2^5 + 0 \times 3^5 + 5 \times 4^5 + 1 \times 5^5 + 6 \times 6^5 + 0 \times 7^5 + 1 \times 8^5$. Since it is evident that when the minimum decomposition of N is known, a decomposition of $(N+1)$ can be obtained merely by adding 1^5, space can be saved by omitting the entries for those numbers for which this decomposition is the minimum one. This has been done here, with the result that the numbers up to 10,000 occupy only about 1050 entries, and are set out in four and a half pages. After 150,000 such an entry as

179379	12

means that 12 fifth powers will suffice for this number. The actual decomposition is quite easy to find: subtracting 11^5 or 161051 from 179379 gives 18328, which (from the earlier part of the table) has more than 11 decompositions. Hence the first term is not 11^5. Next taking 10^5 as a trial value, we find from the table that 79379 has too many decompositions. The next trial, with 2×9^5, leaves a remainder $61281 = 3^5 + 4 \times 4^5 + 3 \times 6^5 + 2 \times 7^5$, making the correct total of 12 fifth powers for the original number.

The number of fifth powers to be added together to make a given integer seems on the whole to decrease with the size of the number. No number in the table requires more than 37 terms, and this occurs only for $N = 223$. After this, no number requires more than 31 fifth powers; after 30,000 no number up to 300,000 requires more than 19; and between 191,263 and 4,037,824 it has been proved that 15 terms will always suffice. It is also interesting to note that the results given here have been used by Dickson to prove that 37 gives an upper limit for numbers right up to 10^{483}.

The book is well printed (it is reproduced by the replica process from typescript, to reduce the risk of error), but it might have been convenient if a table of fifth powers had been printed as an appendix.

J. H. A.